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# Seven-Membered Carbocycle Synthesis By Cobalt-Mediated [3 + 2 + 2] Allyl/Alkyne Cycloaddition Reactions And Novel [5 + 2] Cyclopentadiene/Alkyne Ring Expansions.

by

Trevor L. Dzwiniel

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment
of the requirements for the degree of Doctor of Philosophy.

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*for my parents*

# Abstract

A new reactivity pattern involving the cobalt-mediated cycloaddition of an $\eta^3$-allyl ligand with alkyne molecules is presented. Templates such as $(C_5Me_5)Co(\eta^3\text{-}C_3H_5)(OTf)$ readily yield stable $\eta^5$-cycloheptadienylcobalt complexes from cycloaddition of the allyl ligand with two alkyne molecules, although different alkynes can give rise to various substitution patterns in the product. The alkyne cycloaddition chemistry of several substituted allyl complexes is also investigated. Formation of cycloheptadienyl products is shown to be limited primarily to the reaction of allyl templates with acetylene; larger alkynes lead to the formation of five-membered rings from a related [3 + 2] cycloaddition process. Alkyl substituted allyl ligands react with acetylene to produce $\eta^5$-cycloheptadienylcobalt complexes using not only the $\eta^5\text{-}C_5Me_5$ ancillary ligand, but also the more available cyclopentadienyl complex. In particular, exocyclic cobalt allyl complexes readily form fused bicyclic $\eta^5$-cycloheptadienylcobalt products. Several mechanistic proposals are presented for the cycloaddition process.

The synthetic viability of this reactivity pattern is dependent upon the facile removal of the newly formed carbocyclic system from the metal template. This is accomplished by the addition of a mild carbon nucleophile, which generates an ($\eta^4$-cycloheptadiene)cobalt complex. These diene complexes are readily demetallated without diene isomerization using the mild oxidant $Cp_2Fe^+ PF_6^-$, forming cycloheptadiene ring systems.

A brief investigation into the anomalous reactivity patterns of disubstituted alkynes with the $(\eta^5\text{-}C_5H_5)Co(\eta^3\text{-}C_3H_5)$ template evolved into the development of a conceptually new cycloaddition pathway. A cyclopentadiene ligand, a strong protic acid, and an alkyne combine at a cobalt center to form a new $\eta^5$-cycloheptadienyl ligand. A mechanistic proposal that involves carbon-carbon bond activation of the unactivated cyclopentadiene ligand is presented.

Several alkyl substituted cyclopentadiene complexes are assayed for this reactivity pattern; the ($\eta^5$-$C_5H_5$)Co($\eta^4$-*t*-Bu$C_5H_5$) template demonstrates the greatest overall selectivity for the formation of single ($\eta^5$-*t*-Bu$C_5H_4$)Co($\eta^5$-cycloheptadiene) products. Cyclopentadienyl templates which have substituents on both rings also participate in this reactivity pattern. Although a slightly greater tolerance for alkyne substituents effects is noted, these templates produce a number of isomeric products.

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## List of Abbreviations

| | |
|---|---|
| Å | Angstrom |
| APT | Attached Proton Test |
| Bz | Benzyl |
| COSY | Correlated Spectroscopy |
| Cp | $\eta^5$-cyclopentadienyl |
| Cp* | $\eta^5$-pentamethylcyclopentadienyl |
| Cp' | $\eta^5$-methylcyclopentadienyl |
| Cp$^t$ | $\eta^5$-*t*-butylcyclopentadienyl |
| Cp$'^t$ | $\eta^5$-*t*-butyl-methyl-cyclopentadienyl |
| DGM | Davies-Green-Mingos rules |
| DMAD | Dimethyl acetylenedicarboxylate |
| DQF | Double Quantum Filtered |
| equiv | Equivalents |
| EWG | Electron withdrawing group |
| GCOSY | Gradient COSY |
| $H_a$ | Allyl anti proton |
| $H_c$ | Allyl central proton |
| $H_s$ | Allyl syn proton |
| HETCORR | Heteronuclear Chemical Shift Correlation |
| HMBC | Heteronuclear Multiple Bond Coherence |
| HMQC | Heternuclear Multiple Quantum Coherence |
| Hz | Hertz |
| L | Ligand |
| M | Metal |
| Me | Methyl |
| MO | Molecular Orbital |
| Ms | Methanesulfonate (mesylate) |
| NMR | Nuclear Magnetic Resonance |
| NOE | Nuclear Overhauser Effect |
| OAc | Acetate |
| ORTEP | Oak Ridge Thermal Ellipsoid Plot |
| OTf$^-$ | Trifluoromethanesulfonate (triflate) |
| Ph | Phenyl |
| Pr | Propyl |
| R | Alkyl Group |

| | |
|---|---|
| S | Solvent |
| Tp* | Tris(3,5-dimethylpyrazolyl)borane |
| TBDMS | t-Butyldimethylsilyl |
| TFE | 2,2,2-trifluoroethanol |
| THF | Tetrahydrofuran |
| TMS | Trimethylsilyl |

# Chapter 1. Overview of Metal-Mediated Cycloaddition Processes Used in the Synthesis of Seven-Membered Ring Systems.

## *A. General Metal-Mediated Cycloaddition Reactions*

Transition metal-mediated cycloaddition reactions are among the most important applications of organometallic chemistry to organic synthesis.[1-3] Cycloaddition reactions are a particularly efficient method of constructing cyclic or polycyclic systems in which the number of rings formed and the ring size(s) can be controlled.[4-7] Transition metal complexes are capable of performing cascades of consecutive transformations, resulting in the creation of several carbon-carbon bonds from a particular substrate or substrates.

For the purpose of this discussion, metal-mediated transformations resulting in a cyclic product may be classified as either a cycloaddition or cyclization process. A cycloaddition reaction may be defined as a transition metal-mediated process whereby two or more separate molecules or fragments of a molecule are transformed into a single carbocyclic product on a metal template. The metal complex may or may not be a part of the final product. Cyclization, in contrast, is the conversion of a single polyunsaturated molecule into a cyclic product by a transition metal complex, without the inclusion of fragments, such as CO, from the metal complex. An intramolecular cycloaddition may be confused with a cyclization process; however, the intramolecular cycloaddition must generate a new ring that would not be formed in the absence of the tether.

Methodology for transition metal-mediated construction of small (3-4-membered) and medium (5-6-membered) carbocyclic ring systems is reasonably well developed. Iron carbene complexes, for example, are well known to cyclopropanate alkenes in a [2 + 1] cycloaddition process.[8,9] An example of four-membered ring synthesis is the metal catalyzed [2 + 2] cycloaddition reaction of strained alkenes with alkynes to form a cyclobutene system.[10] Five-membered rings are readily synthesized using, for example, the Pauson-Khand reaction, which creates cyclopentenones by "condensation" of an alkene, an alkyne, and carbon monoxide.[11] Generally, the Pauson-Khand reaction is mediated by cobalt complexes, although several other metals are also reactive.[12] Both monocyclic and bicyclic products can be prepared, the latter by an intramolecular version of the reaction. Catalytic Pauson-Khand reactions have also been recently developed using cobalt and rhodium systems.[13]

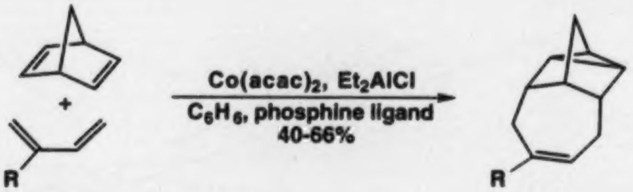
Transition metal-mediated cycloaddition processes leading to six-membered rings are more widely used. The Diels-Alder reaction occurs under much milder conditions than required for the thermal reaction when a metal catalyst is employed.[14] The reaction of molybdenum or chromium vinyl carbene complexes with dienes is also used to form six-membered rings.[15] The metal-mediated [3 + 2 + 1] cyclization of a vinyl carbene, an alkyne and carbon monoxide to give phenols (the Dötz reaction) is also well known.[16]

One of the more impressive reactions mediated by certain transition metals is the condensation of three alkyne molecules to form a substituted benzene ring. Cyclotetramerization of alkynes by metal complexes is also known to occur, forming cyclooctatetraenes.[17] The former process is readily adaptable, thus, cycloadditions of one alkene with two alkynes or a diyne to produce cyclohexadienes are equally facile, as are co-cyclizations of one nitrile and two alkynes. Vollhardt and others have extensively reviewed the alkene/alkyne cyclotrimerization chemistry catalyzed by transition metal complexes.[18] Recent advances by Takahashi demonstrate the use of three different alkynes to form polysubstituted benzene rings in a controlled stepwise transformation.[19a] Other recent advances in the mechanism and development of this chemistry have been published.[19]

Synthesis of seven-membered carbocycles through metal mediation is much less established and many of the existing seven-membered ring syntheses are specific to one or, at most, a few examples. Some illustrative cyclization processes have recently been used successfully to form seven-membered ring products. Ring closing olefin metathesis, although often used for the synthesis of medium size cyclic systems, has not been appreciably used for the synthesis of seven-membered rings and only a handful of examples has been reported.[20] The Heck reaction has been used only rarely in seven-membered ring synthesis.[21] Alper has used a variation of the Heck reaction in a palladium catalyzed synthesis of seven-membered ring lactams.[22] Nickel catalyzed cyclization of dienones or enones has been shown to form seven-membered rings.[23] Finally, Liebeskind has reported a rhodium catalyzed rearrangement of cyclopropylcyclobutenone compounds to cycloheptadienones.[24]

Cycloaddition methodology, in contrast, is seldom used in the formation of seven-membered ring products. Several classes of natural products such as ingenanes and phorbol esters contain seven-membered rings, and this observation has been a driving force for the creation of new metal-mediated methodology for the synthesis of such carbocycles.[25] The methods used in the metal-mediated synthesis of seven-membered rings vary from two component condensations (*e.g.*, [4 + 3] cycloadditions) to transformations of a single acyclic chain to cycloadditions of three or more sub units.

Cobalt catalyzed [$4\pi + 2\pi + 2\pi$] homo Diels-Alder reactions of norbornadiene with dienes have been observed to form polycyclic cycloheptenes (Eq. 1).[26] This process

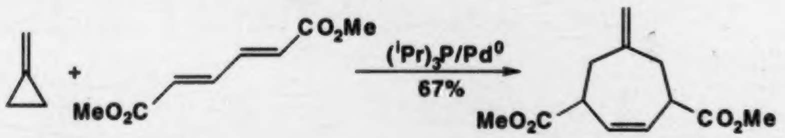


(Eq. 1)

would normally yield an eight-membered ring; however, the norbornadiene bridgehead carbon interferes, and a slightly altered rearrangement takes place. Intramolecular [4 + 2 + 2] cycloaddition reactions yielding tricyclic systems with a seven-membered ring have been reported.[27] Other higher-order cycloaddition processes yielding polycyclic seven-membered ring containing compounds have also been reported.[28,29] A few metal-mediated cycloaddition strategies have received greater attention; these are surveyed below.

### *B. [4 + 3] Metal-Mediated Cycloaddition Processes*

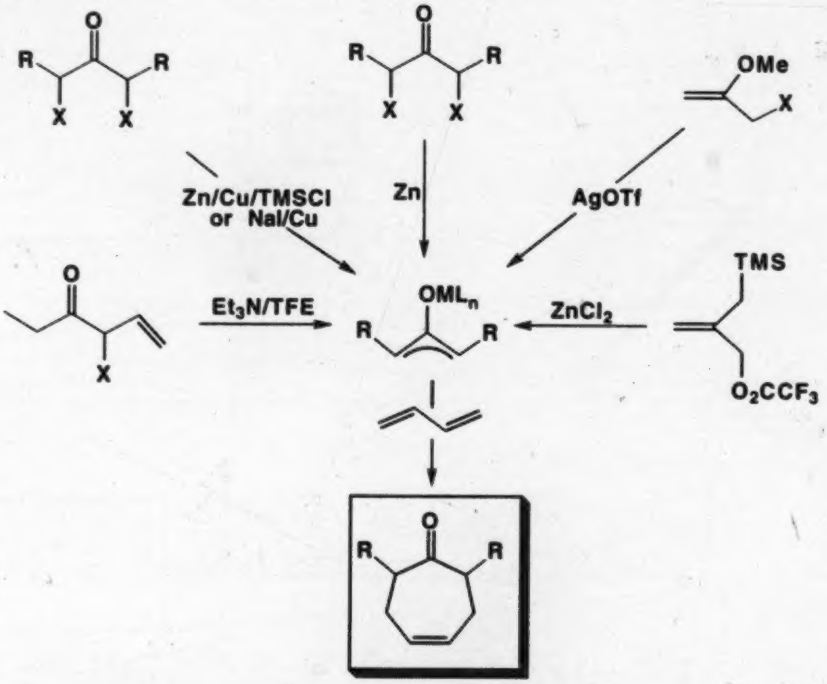
Formation of a larger ring system is possible by metal-mediated insertion of unsaturated molecules into cyclopropane rings. However, nickel or palladium catalyzed condensations of carbon monoxide with multiple molecules of methylenecyclopropane or cyclopropene generally show poor selectivity for seven-membered rings.[30] One exception is seen in a palladium catalyzed cycloaddition of methylenecyclopropane with the dimethyl ester of muconic acid to form a seven-membered ring (Eq. **2**), presumably via a palladium trimethylenemethane intermediate and a [4 + 3] cycloaddition process.[30,31]



(Eq. 2)

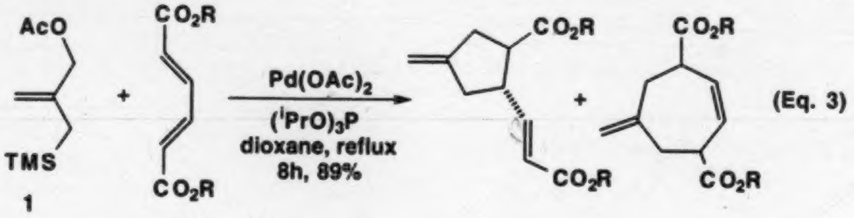
One of the first general methods developed to synthesize seven-membered rings is the $Fe_2(CO)_9$[3,32] or Zn[33] mediated reduction of α, α'-dihaloketones in the presence of a diene. An oxyallyl complex, generated by the reduction of the dihaloketone, is trapped by the diene and undergoes a [4 + 3] cycloaddition reaction to form cycloheptenone products. Due to the toxicity of both dihaloketones and the iron carbonyl complex, several other routes to oxyallyl cations have more recently been developed (Scheme **1**), extending the utility of this reactivity pattern. Examples include the solvolysis of allylic halides in strongly ionizing solvents and ionization of a halo enol ether. Other research groups have developed metal-free methods of forming oxyallyl intermediates for use in intramolecular seven-membered ring formation. Several early reviews on the mechanistic pathways[34] and synthetic utility[35] are available, as well as updated reviews[36] covering intramolecular variations[37] and recent applications.[38]

**Scheme 1**



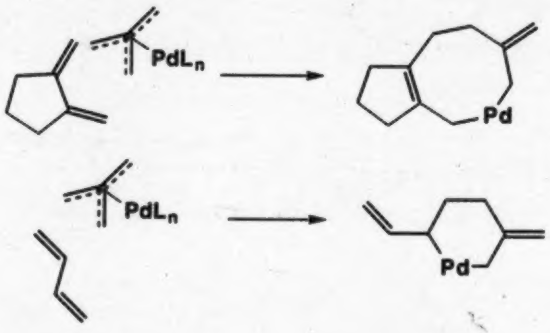
One valuable characteristic of this reaction is the ability to use furans, pyrans, and even benzene as a diene source to form a variety of bridged seven-membered ring products. However, the ring skeleton of the product is limited to cyclohept-4-en-1-ones. This reaction does not allow direct production of highly unsaturated seven-membered rings and only a limited range of substitution patterns is accessible.

Trost has also made considerable advances in seven-membered ring synthesis with the use of trimethylenemethane ligands.[31,39] Catalytic amounts of $Pd(OAc)_2$ and $(^iPrO)_3P$, when allowed to react with trimethylenemethane precursor **1** and a diene, yield a mixture of both five- and seven-membered rings (Eq. 3). Typically only 20-50% of the product mixture is composed of the seven-membered ring and the material balance is composed of cyclopentane structures.

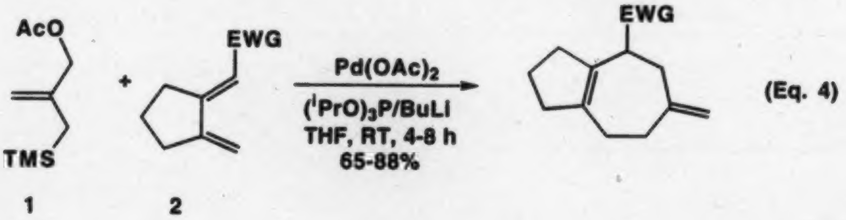

AcO
TMS
1
CO₂R
CO₂R
Pd(OAc)₂
(ⁱPrO)₃P
dioxane, reflux
8h, 89%
CO₂R
CO₂R
CO₂R
CO₂R
(Eq. 3)

Bicyclic seven-membered ring systems can be produced with much higher selectivity when the rotational freedom of the diene is restricted. This forces the transition state into a geometry favoring a [4 + 3] cycloaddition (Figure 1), whereas a freely rotating diene is more likely to adopt a conformation preferable for a [3 + 2] cycloaddition process.

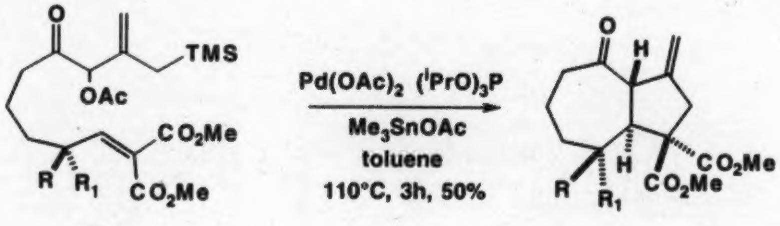
**Figure 1.** Transition State Approach in [4 + 3] vs [3 + 2] Cycloaddition Reactions


PdLₙ
Pd
PdLₙ
Pd

Thus, selectivity for seven-membered rings is dramatically improved[40] using bis(methylene)cyclopentanes **2**, which are fixed into a *cisoid* arrangement (Eq. **4**).


AcO
TMS
1
EWG
2
Pd(OAc)₂
(ⁱPrO)₃P/BuLi
THF, RT, 4-8 h
65-88%
EWG
(Eq. 4)

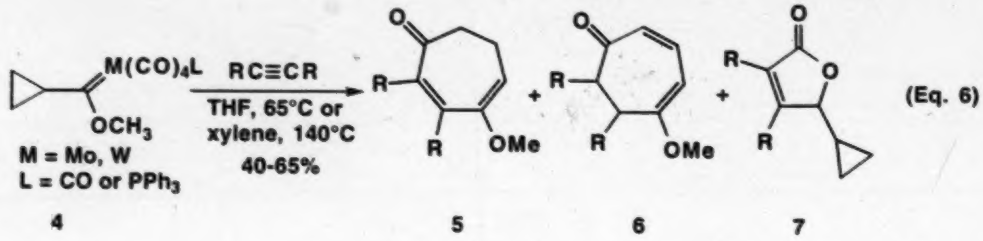
An intramolecular approach also allows high conversions of unsaturated acyclic molecules to bicyclic [5.3.0] systems using this palladium catalyzed methodology (Eq. 5).[41] Both the trimethylenemethane and an activated alkene are incorporated into a single chain (**3**) and subjected to the cyclization procedure, using trimethyltin acetate as a co-catalyst. This intramolecular [3 +2] cycloaddition gives seven-membered cyclization products when the tether is of appropriate length. This procedure has previously been used to form [3.3.0] octane and [4.3.0] nonane systems.[42] Variation of the tether length between the two ends of the chain allows for the production of different [n.3.0] systems, as the larger ring is formed by fusing the ends of the tether. However, the concept of an intramolecular [4 + 3] reaction by way of a trimethylenemethane precursor is also feasible, if not proven.



**3**

(Eq. 5)

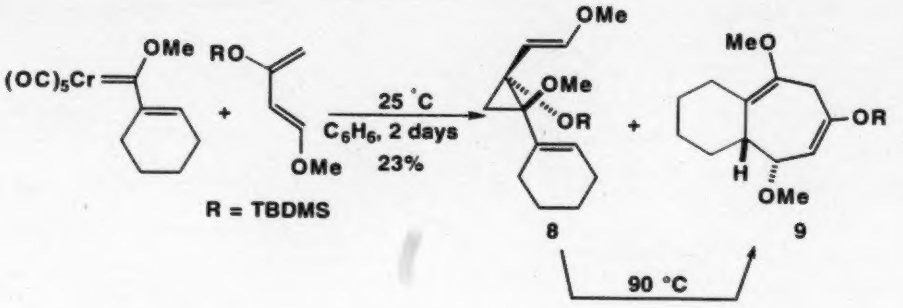
Herndon[43] has shown that cycloheptadienones are sometimes formed in a [4 + 2 + 1] cycloaddition process when cyclopropylcarbene carbonyl complexes **4** (L = CO or $PPh_3$) are allowed to react with alkynes (Eq. **6**), although this reaction usually forms six-membered carbocycles in a Dötz cyclization process.[16] Generally, two isomers (**5** and **6**) are obtained in this process, although greater amounts of the thermodynamically more stable **6** can be obtained using a longer reaction time and higher temperature. Substituents on the alkyne are limited to alkyl, aryl or silyl groups. In order for the seven-membered ring to form, a specific sequence of steps must occur, despite several other competing reaction pathways. One such pathway, the production of furanone **7**, appears to be suppressed by the use of the $PPh_3$ complex. However, these side reactions severely limit the utility of this process for the synthesis of seven-membered rings.



### *C. Rearrangement of Divinylcyclopropanes From Metal-Mediated Processes*

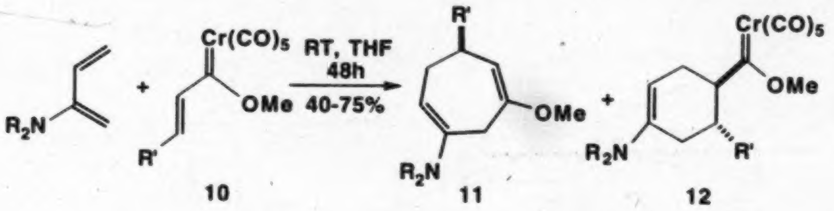
Several groups have developed approaches to seven-membered rings by the use of metal-mediated syntheses of divinylcyclopropanes. These molecules, particularly the *cis* divinylcyclopropane systems, are known to undergo thermal rearrangement to cycloheptadienes at very mild temperatures (via the Cope rearrangement).[44] *Trans*-divinylcyclopropanes are considerably more robust, yet do convert slowly upon heating or photolysis. It is proposed that the *trans* isomer either first epimerizes to the *cis* form, then undergoes the Cope rearrangement, or that the *trans* isomer rearranges via a diradical process.

Metal-mediated formation of divinylcyclopropane systems has been known for some time. Chromium vinylcarbene complexes are used by Wulff to cyclopropanate dienes.[9b,45] From a reaction at room temperature, a mixture of **8** and **9** is isolated (Eq. 7). Presumably, the *cis*-divinylcyclopropane product rearranges under the reaction conditions to compound **9**, while the *trans*- form is isolable, although on mild heating, **8** converts to **9**. The reaction is metal-specific; only chromium carbenes have been observed to form these products. The corresponding tungsten carbene system yields products from a [4 + 2] cycloaddition reaction. This particular example is also highly specific: all other changes to the diene or carbene complex lead exclusively to [4 + 2] reaction products.



(Eq. 7)

Other vinyl carbene mediated reactions are used by Barluenga to form seven-membered ring products (Eq. **8**).[46] Use of 2-aminobutadienes and chromium carbene **10** allows good (10:1) selectivity for seven-membered ring over cyclohexene products. Dramatic metal-dependence on the reaction pathway is again observed as only the chromium carbene forms compounds such as **11**; molybdenum carbene complexes yield only the Diels-Alder adducts (**12**). Asymmetric synthesis of the seven-membered carbocycle is possible using a diene containing a chiral auxiliary on the nitrogen atom.

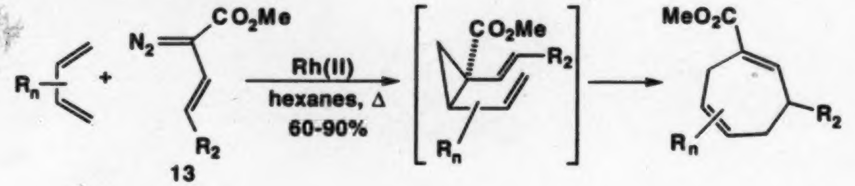


(Eq. 8)

Azepines are also readily synthesized using this method, by replacing the aminobutadiene with 4-amino-1-azadienes. Enantioselectivity can be induced by using a menthol ether group on the carbene. Formation of the azepines occurs under mild conditions (-40°C) in contrast to the room temperature conditions required for most other carbene reactions.

In spite of the apparent efficiency of the above carbene methods, relatively few examples have been demonstrated. Difficulty in finding reactive metal carbene precursors, side reactions and incomplete reactions all combine to render these procedures somewhat limited. Reaction of unsaturated carbenes with dienes normally yields [4 + 2] cycloadducts. The same metal reagents can also lead to combination of an unsaturated carbene, a CO ligand, and an external alkyne source to form benzene rings (the Dötz reaction).[16]

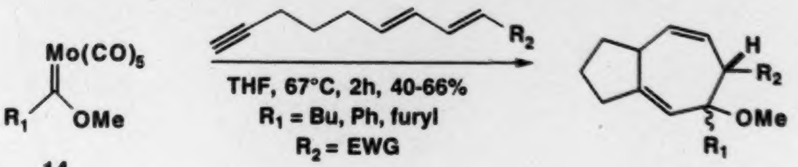
Davies has shown that using rhodium catalysts to decompose carbene precursors in the presence of dienes also forms seven-membered rings.[47,48] Rhodium (II) species are known to convert vinyldiazomethanes **13** to rhodium stabilized carbenoid species. These poorly defined carbenoid complexes readily cyclopropanate dienes, forming divinylcyclopropane intermediates (Eq. **9**). As usual, a Cope rearrangement ultimately produces the cycloheptadienes.



(Eq. 9)

This approach is more widely applicable, since the diene can be varied from simple acyclic dienes to cyclopentadiene(s), pyrroles, furans and benzenes. Recent development in this area has focused on enantioselective and diastereoselective methodology using chiral rhodium (II) catalysts to perform asymmetric synthesis. Padwa[49a,b] has used this rhodium carbenoid process to form several rings in a single intramolecular reaction leading to polycyclic cycloheptadiene products. The decomposition of α-diazocarbonyl compounds by Rh(II) in the presence of aromatic systems has been used to synthesize seven-membered ring compounds in a formal [6 + 1] cycloaddition process.[49c]

Other variations of using carbene complexes to form seven-membered rings through transient divinylcyclopropanes were demonstrated by Harvey (Eq. **10**).[50] The metal carbene **14** undergoes a [2 + 2] metathesis reaction preferentially with the alkyne to form an intermediate vinyl carbene. A further metathesis reaction with the internal olefin closes the five-membered ring. Reductive elimination to a divinylcyclopropane occurs, followed by the standard Cope rearrangement. This method suffers from low yields of

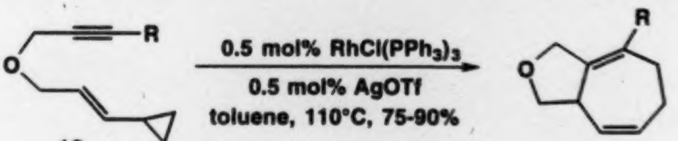


**14** **15** (Eq. 10)

the hexahydroazulene product (*e.g.*, **15**) and also from several competing reactions. Unless $R_1$ is a phenyl, butyl or furyl group, other compounds such as acyclic dienals, cyclopentenones and Dötz reaction products predominate. Only in these few cases are the hexahydroazulene complexes **15** obtained. A more complicated tricyclic fused ring system has been prepared using an intramolecular variation of this method, in which a long alkoxy side chain replaces the methoxy group. Alkyne and diene fragments are introduced into the chain at key positions.[51]

### D. *[5 + 2] Metal-Mediated Cycloaddition Processes*

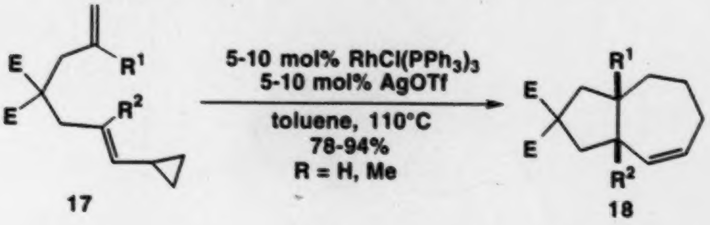
Although the use of a [4 + 3] type reaction pathway may be the most prevalent method of seven-membered ring synthesis, other methodologies have also been developed. Wender recently reported a rhodium-catalyzed [5 + 2] cycloaddition process that generates various seven-membered ring compounds (Eq. **11**).[52] The reaction tolerates variation of the substrate and a wide range of alkyl groups has been successfully



**16** (Eq. 11)

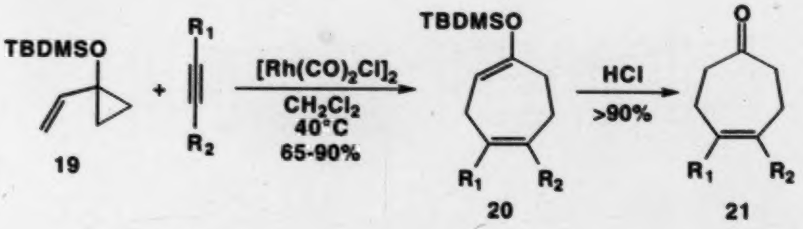
used. The ether linkage in compound **16** can be replaced by $C(CO_2Me)_2$ without a significant change in reactivity, leading to the production of carbocyclic [5.3.0] products.

Other results from Wender further expand the scope of this reactivity pattern. Replacement of the alkyne with an alkene in the substrate permits the formation of bicyclic cycloheptenes **18** in good yield. Interestingly, this intramolecular cycloaddition produces only one diastereomer at the ring fusion: the *cis* isomer.



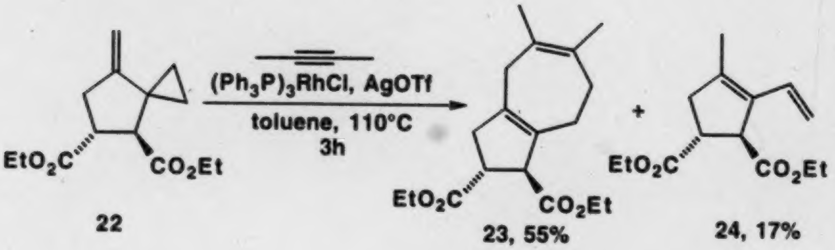
(Eq. 12)

This reaction has very recently been reported in an intermolecular form using vinylcyclopropane **19**, an alkyne and a rhodium carbonyl catalyst.[53] This particular set of conditions exhibits a large tolerance for electronic changes in the alkyne; nearly all variations provide cycloadducts **20**, which are readily hydrolyzed to cycloheptenones **21**. The reaction is tolerant of various functional groups on the alkyne including esters, ketones, ethers and alcohols.



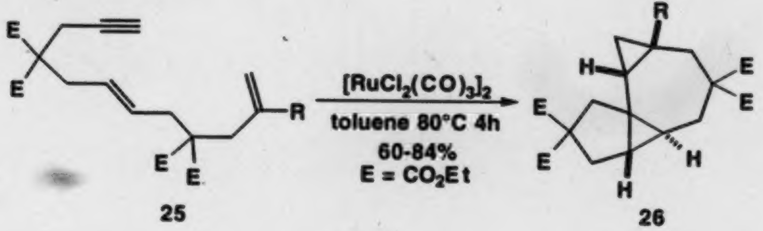
(Eq. 13)

Binger has recently demonstrated a closely related [5 + 2] cycloaddition reaction involving a vinylcyclopropane and an alkyne.[54] Using the same *in situ* generated rhodium triflate complex seen in Eqs. **11** and **12**, "$(Ph_3P)_3Rh(OTf)$", in toluene at reflux, vinylcyclopropane **22** reacts with 2-butyne to generate the bicyclic complex **23** (Eq. **14**). This process is less selective; two unidentified isomers of the major complex are also produced, as well as a substantial amount (17%) of vinylcyclopentene, from cyclopropane ring opening without cycloaddition of the alkyne.



(Eq. 14)

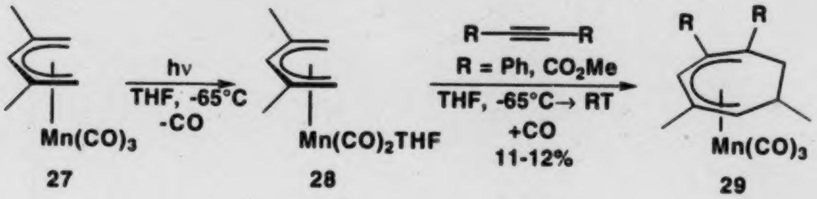
Murai has demonstrated the cyclization of linear polyunsaturated substrates as well, employing a ruthenium catalyst to effect a complex cyclization of dienyne **25** to the tetracyclic framework **26**.[55] The stereocontrol of this reaction is very good; only a single stereoisomer is observed in 60-84% yield. The reaction is quite sensitive to olefin geometry and any changes to the internal olefin give rise to complicated product mixtures. Several different transition metal complexes ($PtCl_2$, $[RuCl_2(CO)_3]_2$, $[Rh(O_2CCF_3)_2]_2$) catalyze this cyclization, demonstrating an unusual metal-independence in a metal-mediated synthesis of seven-membered rings. Although the ruthenium catalyst generally gives the highest yield, only $[Rh(O_2CCF_3)_2]_2$ yields the desired product when the R group is chloride.



(Eq. 15)

Kreiter has shown that [5 + 2] cycloaddition reactions involving ($\eta^5$-pentadienyl)manganese tricarbonyl and an alkyne, such as diphenylacetylene or DMAD, yield seven-membered ring products (Eq. **16**).[56] The stable pentadienyl complex **27** must first be photolytically activated, forming the thermally unstable tetrahydrofuran complex

**28**. The THF complex **28** then reacts thermally with excess alkyne, providing the cycloadducts **29**, albeit in very poor yield.

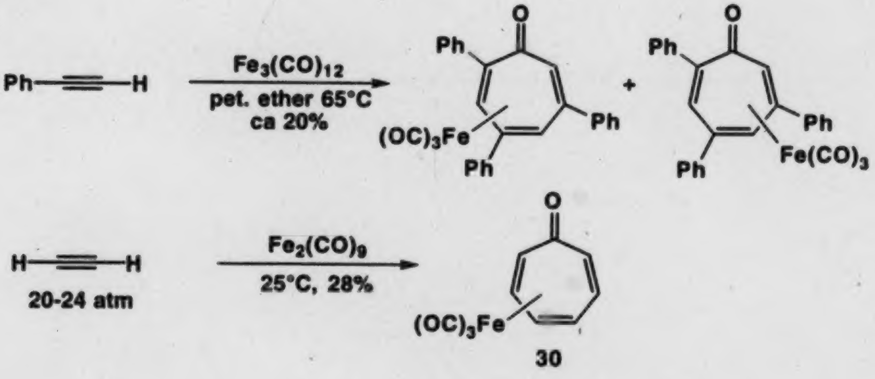

hν
THF, -65°C
-CO
Mn(CO)3
27
Mn(CO)2THF
28
R—≡—R
R = Ph, CO2Me
THF, -65°C→ RT
+CO
11-12%
R
R
Mn(CO)3
29

(Eq. 16)

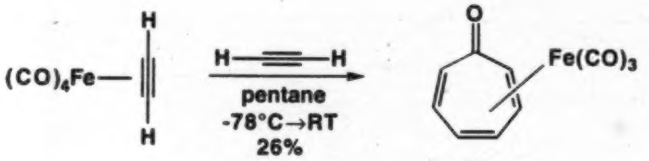
### *E. Multicomponent Cycloaddition Processes Forming Seven-Membered Rings*

Most cycloaddition reactions that form seven-membered rings are two component reactions or involve intramolecular tethering to control the reaction of multiple unsaturated moieties. There is only a handful of examples of metal-mediated intermolecular multicomponent cycloaddition reactions that form seven-membered rings, most discovered serendipitously. Hubel has reported several examples of a [2 + 2 + 2 + 1] cycloaddition using an iron carbonyl compound and several acetylenes (Scheme **2**).[57] This reaction requires a terminal acetylene (HCCH, PhCCH, *p*-BrPhCCH) and is accompanied by several byproducts, giving low yields of the coordinated tropones.

**Scheme 2**


Ph—≡—H
Fe3(CO)12
pet. ether 65°C
ca 20%
O
Ph
Ph
Ph
(OC)3Fe
+
O
Ph
Ph
Ph
Fe(CO)3
H—≡—H
20-24 atm
Fe2(CO)9
25°C, 28%
O
(OC)3Fe
30

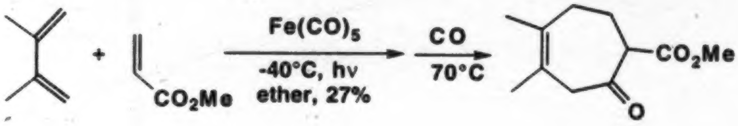
Recently, Takats has reported a synthesis of tropone complex **30** starting from a preformed iron alkyne complex (Eq. **17**).[58] This alkyne complex could conceivably be an intermediate in Hubel's chemistry. The yield is similarly low, but no other isolable products are reported.



**30**

(Eq. 17)

One other iron-mediated multi-component cyclization has been described.[59] Grevels has prepared cycloheptenone **31** from the cyclization of a diene, an alkene, and carbon monoxide in a *formal* [4 + 2 + 1] cycloaddition reaction (Eq. **18**), although the overall process requires multiple steps and the yield of the final thermolysis step is not given. Other products reportedly form, but no byproducts have as yet been identified.

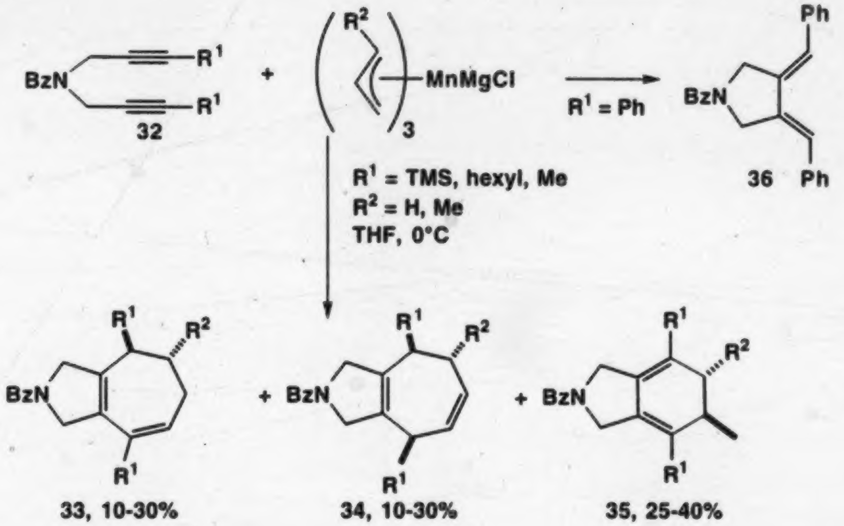


**31**

(Eq. 18)

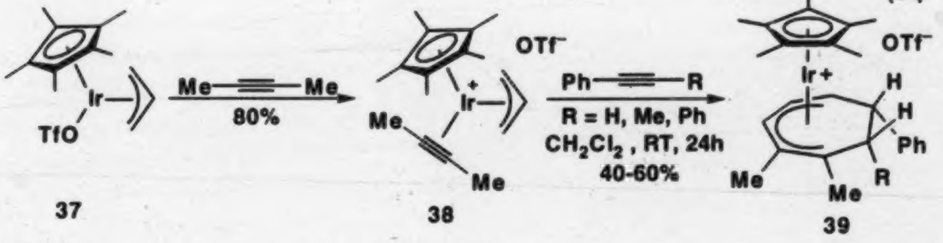
Remarkably, there are very few metal-mediated cycloaddition reactions that transform isolable metal allyl compounds into seven-membered rings. During the course of our investigation, Oshima reported a manganese-mediated cyclization of a diyne substrate **32** to form seven-membered rings **33** and **34** as well as a six-membered ring product **35** (Scheme 3).[60] The reaction suffers from low yields and poor generality. Only diynes with terminal alkyl or trimethylsilyl groups afford seven-membered rings; substrates with terminal phenyl groups form bismethyleneazacyclopentane **36**, in which the alkynes have reacted without incorporation of the allyl.

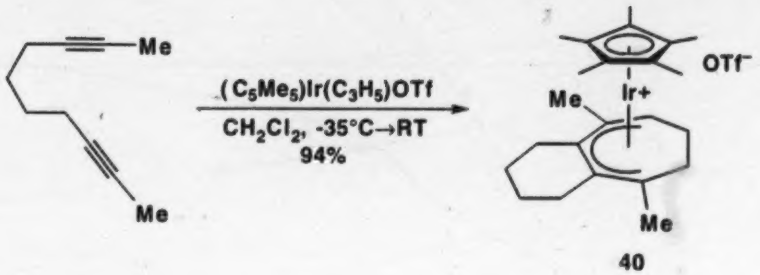
Scheme 3


BzN
R$^1$
32
+
R$^2$
MnMgCl
3
R$^1$ = Ph
Ph
BzN
36
R$^1$ = TMS, hexyl, Me
R$^2$ = H, Me
THF, 0°C
33, 10-30%
34, 10-30%
35, 25-40%

Some years earlier, Stryker demonstrated the feasibility of iridium mediated [3 + 2 + 2] allyl/alkyne cycloaddition reactions.[61] In this process, the iridium allyl triflate complex **37** coordinates 2-butyne to form isolable allyl alkyne complexes **38**, which react further with excess alkyne to form $\eta^5$-cycloheptadienyl complexes **39** (Eq. **19**). The iridium allyl triflate complex **37** also reacts with an $\alpha,\omega$-diyne to form the bicyclic cycloheptadienyl complex **40** (Eq. **20**). The use of iridium in this method necessarily limits it to a demonstration model, due to the prohibitive cost of stoichiometric iridium. In addition, difficulties were incurred in attempts to remove the ring system from the metal.[62]

(Eq. 19)


Ir
TfO
37
Me—≡—Me
80%
OTf$^-$
Ir
Me
Me
38
Ph—≡—R
R = H, Me, Ph
CH$_2$Cl$_2$ , RT, 24h
40-60%
OTf$^-$
Ir+
H
H
Ph
R
Me
Me
39



**40**

(Eq. 20)

### *F. Project Goals*

With the limitations of the iridium system in mind, our goal was to develop an analogous cobalt-mediated [3 + 2 + 2] cycloaddition, re-creating the iridium-based reactivity manifold and developing synthetically useful methodology to make organic seven-membered ring compounds, avoiding the prohibitive cost of iridium. In this work, we have shown that cobalt mediated [3 + 2 + 2] allyl/alkyne cycloaddition reactions proceed readily to give cycloheptadienyl complexes analogous to the iridium complex **40**, in a reaction much more amenable to future synthetic applications. Extended functionality is introduced into the ($\eta^5$-cycloheptadienyl)cobalt products through the stereoselective addition of carbon nucleophiles and the resulting functionalized $\eta^4$-cycloheptadiene complexes are readily demetallated *via* oxidative processes.

During these investigations, an unanticipated and highly unusual reactivity pattern was discovered, leading to seven-membered ring products in which a skeletal rearrangement has occurred, redistributing the allyl carbons to non-adjacent positions. This serendipitous C-C bond activation process has been developed into a conceptually new reaction in which $\eta^4$-cyclopentadiene cobalt complexes are transformed into $\eta^5$-cycloheptadienyl products by reaction with a proton and an alkyne. This unprecedented and general transformation encompasses several seemingly disparate areas of chemistry, from migratory insertion reactions to agostic complexes and the cleavage of carbon-carbon bonds.

# Chapter 2. [3 + 2 + 2] Allyl/Alkyne Cycloaddition Reactions of Cobalt Complexes.

## I. Introduction and Background

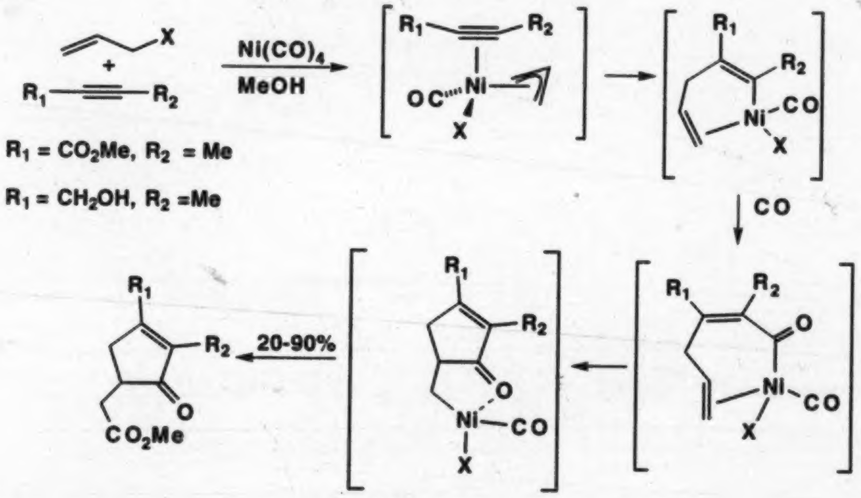
### A. *Reactivity of Intermediate $\eta^3$-Allyl Complexes with Alkynes*

Transition metal allyl compounds show diverse reactivity patterns[1,36c,63] and, in particular, the reactions of alkynes with allyl complexes are of great interest. Only a few isolable transition metal allyl/alkyne compounds have been reported, as such complexes generally undergo further migratory insertion reactions.[61,64] Many transition metal catalyzed condensation reactions of alkynes with allylic precursors are thought to proceed via intermediate allyl complexes, such as the nickel-catalyzed co-oligomerization of alkynes with butadiene.[65,66] A palladium-catalyzed "condensation" of an alkyne with with an allylic carbonate has also been reported.[67] The reactions of $\eta^1$-allyliron complexes with alkynes have recently been reviewed.[68] Other ligands which strongly ressemble allyl ligands have also received a great deal of attention. There has been a substantial amount of work on palladium catalyzed trimethylenemethane/alkene [3 + 2] cycloaddition reactions;[30a,36a,c,69] however, this reaction rarely succeeds with alkynes,[70] except for intramolecular cases.[71]

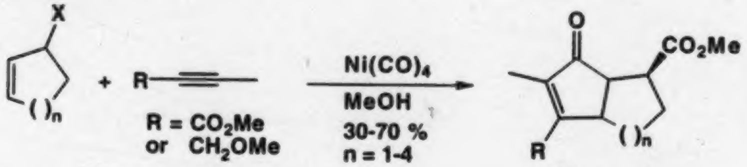
There is also a large body of literature concerned with the chemistry of isolable nickel allyl complexes.[65,72] The vast majority of these reactions, however, deal with alkene chemistry, with alkyne reactivity relegated to a relatively minor position.[72]

One recently developed reaction class involving intermediate allyl/alkyne complexes is the Chiusoli reaction: a series of nickel mediated cycloaddition reactions between an allylic halide, an alkyne and carbon monoxide.[73,74] One of the proposed intermediates, an allyl/alkyne complex, rearranges and undergoes CO insertion to yield an acyl complex (Scheme **4**). This intermediate has not been observed, although it has been implicated by trapping experiments.[75] Although most alkynes can be used in this reaction, the best results are obtained with relatively polarized alkynes such as methyl 2-butynoate or but-2-yn-1-ol. The requirement for alkynes with an electron withdrawing substituent complements the electronic demands of the more well-known Pauson-Khand reaction.[11] In the latter reactivity pattern, electron poor alkynes tend to form a larger percentage of acyclic addition products. Although the Pauson-Khand reaction proceeds using more electron poor alkynes, under such conditions, less control over the regiochemistry of the alkyne insertion is seen and mixtures of isomers are produced.

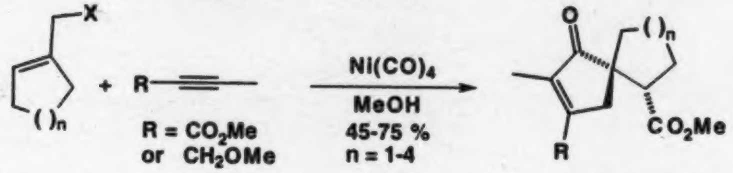
**Scheme 4**



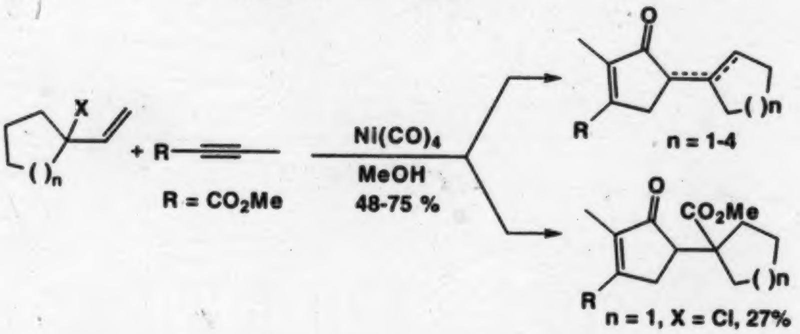
When the structure of the allyl halide is varied, considerably more complicated systems can be synthesized. Cyclopentenones, fused bicyclic cyclopentenones, spirocyclic compounds, and cycloalkenylidenecyclopent-2-enones are all prepared from various allyl precursors, alkynes and CO using these procedures (Eqs. **21-23**). Note that in Eq. **23**, a final β-hydride elimination is favored over CO insertion; only a small amount of the carbonylation product is observed. Many of these reactions are not clean and the major product is accompanied by the formation of other compounds, such as pentadienes or alkyne oligomers. An early review by Chiusoli covers the formation of acyclic products using this process.[73]


X
+
R
( )n
R = CO₂Me
or CH₂OMe
Ni(CO)₄
MeOH
30-70 %
n = 1-4
O
CO₂Me
R
( )n

(Eq. 21)


X
+
R
( )n
R = CO₂Me
or CH₂OMe
Ni(CO)₄
MeOH
45-75 %
n = 1-4
O
( )n
CO₂Me
R

(Eq. 22)


X
( )n
+ R
R = CO₂Me
Ni(CO)₄
MeOH
48-75 %
O
( )n
R
n = 1-4
O
CO₂Me
( )n
R
n = 1, X = Cl, 27%

(Eq. 23)

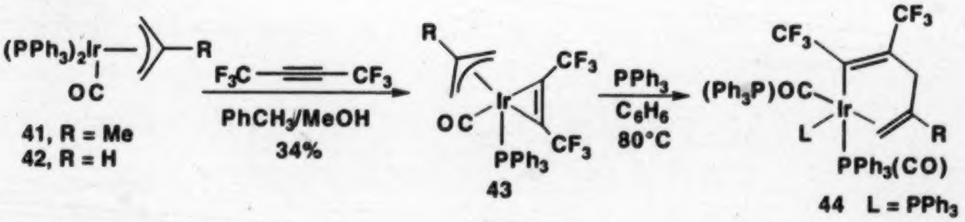
While the Chiusoli reaction is capable of constructing several different types of ring systems, it still requires substantial development. The reaction is not very tolerant of functional groups on the alkyne; good results are generally only obtained with reasonably electron poor alkynes and most successful examples use polarized alkynes. Many byproducts are observed, as $Ni(CO)_4$ can react with alkynes by itself, producing hydroquinones or benzenes from alkyne condensations with or without carbon monoxide. Various acyclic products are also seen from methanolysis of pre-cyclized intermediates. The mechanism, although reasonably well defined, is complex and encompasses diverse pathways, reflecting the many variables involved. Studies thus far have concentrated on expanding the reactivity patterns for use in synthesis, rather than attempting to implicate key intermediates or finding methodology to optimize reaction conditions for other alkynes.

## *B. Reactions of Isolable $\eta^3$-Allyl Complexes with Alkynes*

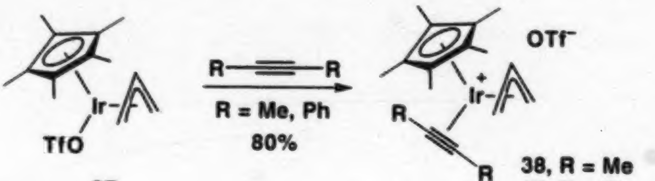
### *1. Isolable Allyl/Alkyne Complexes*

Isolable allyl/alkyne complexes are relatively rare, due to facile migratory insertion rearrangements. However, Green has reported the isolation of an allyl/alkyne complex of iridium, formed by allowing (carbonyl)(methylallyl)-bis(triphenylphosphine)iridium **41** to react with hexafluorobutyne in toluene/methanol solution.[64] An identical reaction is observed to occur with the allyl complex **42** under similar conditions. The allyl/alkyne complex **43** is observed to undergo a migratory insertion reaction upon mild heating (benzene, 80°C) with triphenylphosphine, forming vinyl complex **44** (Scheme **5**).

**Scheme 5**



Schwiebert has also isolated iridium allyl/alkyne complexes and seen even more facile intramolecular migratory insertion chemistry (Eq. **24**).[61,62] Both the alkyne and the allyl triflate precursor **37** are readily soluble in benzene; precipitation of the allyl/alkyne complex **45** occurs upon addition of diethyl ether. Dissolution of **45** in polar solvents causes rapid rearrangement to metallicenium complexes, which will be discussed more fully in later sections. Stable ruthenium allyl/alkyne complexes of the form $(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_2R_2)$ (R = Me, Ph, $SiMe_3$), prepared from Zn reduction of $(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-}C_3H_5)(Br)_2$ with the appropriate alkyne in THF at 0°C, have also been isolated in our group.[76] These complexes thermally rearrange to $\eta^5$-pentadienyl complexes upon mild heating from 0°C to 60°C.



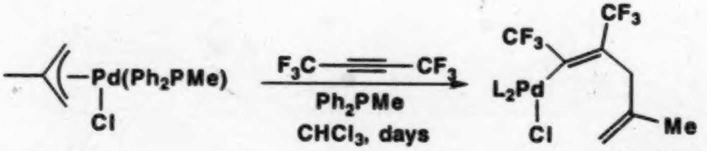
37

38, R = Me
45, R = Ph

(Eq. 24)

## 2. *Allyl/Alkyne Migratory Insertion Reactions*

Reports of single alkyne insertion into *isolable* allyl complexes are also known. Clark has demonstrated a single alkyne insertion into the palladium allyl complex **46**, forming a vinyl olefin ligand (Eq. **25**).[77] The insertion product exists as a mixture of one dimeric and one monomeric structure, the latter with a chelating vinyl olefin ligand. However, addition of another equivalent of phosphine converts both complexes to the monomeric vinyl complex **47**.



46

47 L = Ph$_2$PMe

(Eq. 25)

Similar allyl/alkyne insertion chemistry is seen using iridium complex **48**. Green has observed a single insertion of hexafluorobutyne into an iridium methylallyl complex, again forming a chelating vinyl olefin complex.[64] Ancillary ligand rearrangement occurs in this system, giving a mixture of bis(phosphine)carbonyl **49** and bis(carbonyl)phosphine complex **50** (Scheme **6**). Also present in this mixture is a 1:1 allyl/alkyne adduct **51** that has undergone a *trans* insertion. The analogous allyl complex also inserts one equivalent of alkyne; however, this product appears to arise only from a *trans* insertion of the alkyne, to form exclusively **52**: a structure suggested by the small value of the $J_{FF}$ coupling constant. These *trans* complexes could arise through attack on a free alkyne, in a dipolar transition state (Figure **2**), which then collapses to form the product.

**Scheme 6**

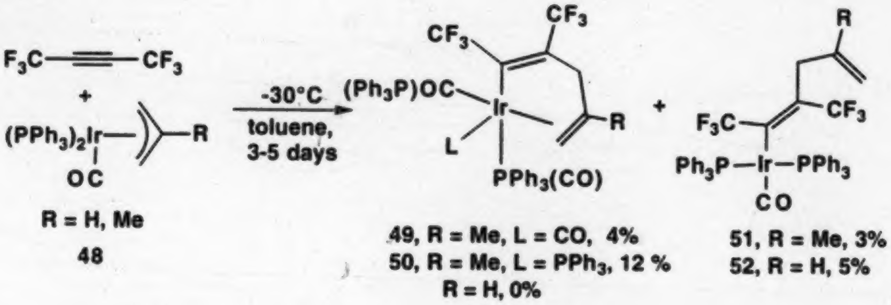
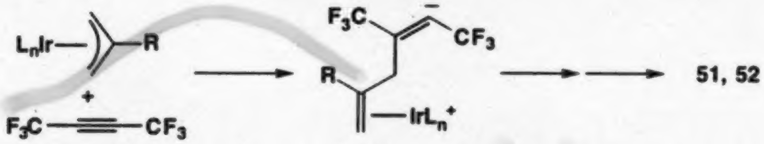
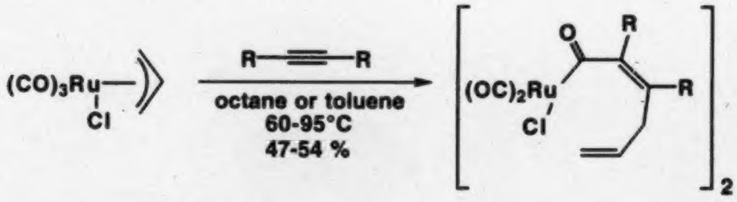

F3C—≡—CF3
+
(PPh3)2Ir
OC
R
R = H, Me
48
-30°C
toluene,
3-5 days
CF3
CF3
(Ph3P)OC
Ir
R
L
PPh3(CO)
+
R
CF3
F3C
Ph3P—Ir—PPh3
CO
49, R = Me, L = CO, 4%
50, R = Me, L = PPh3, 12 %
R = H, 0%
51, R = Me, 3%
52, R = H, 5%

**Figure 2.** Dipolar Transition State for Allyl/Alkyne Insertion Reactions


LnIr
R
+
F3C—≡—CF3
F3C
CF3
R
IrLn+
51, 52

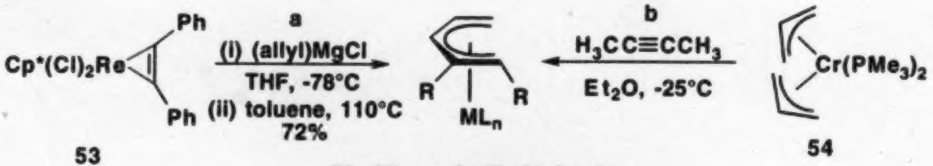
Single alkyne insertion reactions into allyl ligands are also observed for some ruthenium allyl complexes.[78a] In some systems, a further transformation occurs to generate an acyl complex derived from CO insertion into the intermediate vinyl olefin (Eq. **26**). Symmetric alkynes such as acetylene or diphenylacetylene lead to a single dimeric chloro-bridged complex. Unsymmetrical alkynes (phenylacetylene, ethyl propiolate) also undergo insertion to form these dimeric complexes, although the insertion process is not selective, forming a mixture of regioisomers. The relative amount of each isomer is not reported.


(CO)3Ru
Cl
R—≡—R
octane or toluene
60-95°C
47-54 %
O
R
(OC)2Ru
Cl
R
2

(Eq. 26)

Examples of allyl/alkyne addition products that have undergone more extensive ligand reorganization are also known (Scheme **7**). Herrmann,[78b] for example, reports that allowing rhenium alkyne complex **53** to react with allyl magnesium chloride in THF, followed by heating the intermediate in toluene at 100°C, forms an $\eta^5$-pentadienyl complex **55**. A transient allyl/alkyne complex is presumably formed, but no intermediate complexes are characterized. Insertion of the alkyne into the allyl to give a vinyl olefin complex analogous to **47** at room temperature is likely to occur, based on the previous examples. Thermolysis can then effect the C-H activation of a methylene hydrogen in the intermediate vinyl olefin complex, with subsequent reductive elimination yielding the product **55**. Jolly describes a similar rearrangement that forms pentadienyl complex **56** from the chromium complex **54**, but this reaction is observed to proceed under much milder (-25°C) conditions.[79]

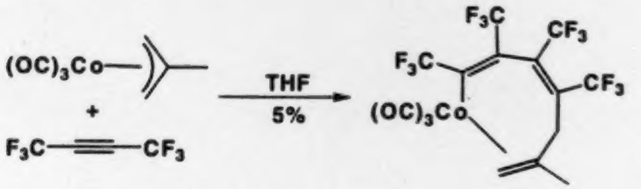
**Scheme 7**



**55**, $ML_n$ = $Cp^*ReCl$, R = Ph
**56**, $ML_n$ = $Cr(\eta^3\text{-allyl})(PMe_3)$, R = Me

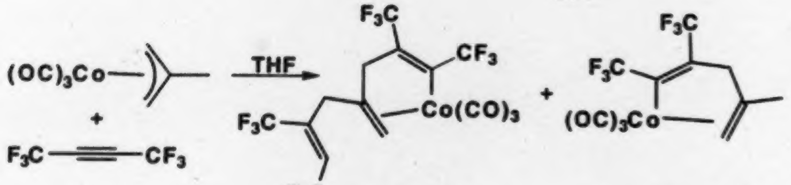
### 3. *Double Alkyne Migratory Insertion Reactions*

Certain systems undergo insertion reactions in which two alkynes are incorporated into the allyl ligand (Eqs **27**, **28**). Stone[80a] and Green[80b] both report products from double alkyne insertion into a cobalt methylallyl complex. The earlier report describes the sequential insertion of two hexafluorobutyne molecules to give complex **57**. Later efforts by Green failed to reproduce this compound, giving instead a different double insertion product (**58**), which forms from the insertion of two alkynes into opposite ends of the methylallyl ligand. In both cases, the products are isolated in low yield, and several other unidentified compounds are formed. It should be noted that Green detects an equal amount of vinyl olefin complex **59** in the crude reaction mixture, generated from a single insertion of alkyne. This reactivity manifold is obviously highly sensitive to small variations in reaction conditions.


(OC)3Co
+
F3C—≡—CF3
THF
5%
F3C
CF3
F3C
CF3
(OC)3Co

(Eq. 27)

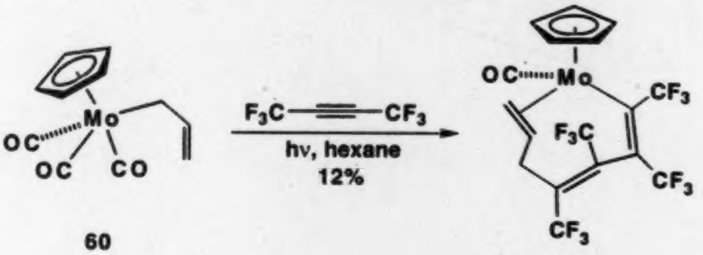
**57**


(OC)3Co
+
F3C—≡—CF3
THF
F3C
CF3
Co(CO)3
F3C
F3C
+
F3C
F3C
(OC)3Co

(Eq. 28)

**58, 18%** **59, 17%**

A molybdenum $\eta^1$-allyl system (**60**) is also reported to insert two equivalents of hexafluorobutyne (Eq. **29**).[81] The initial migration of the allyl generates a *trans* vinyl group, likely from a process similar to that previously described in Figure **2**. A more


Mo
OC
OC
CO
F3C—≡—CF3
hν, hexane
12%
OC
Mo
CF3
F3C
CF3
CF3

(Eq. 29)

**60** **61**

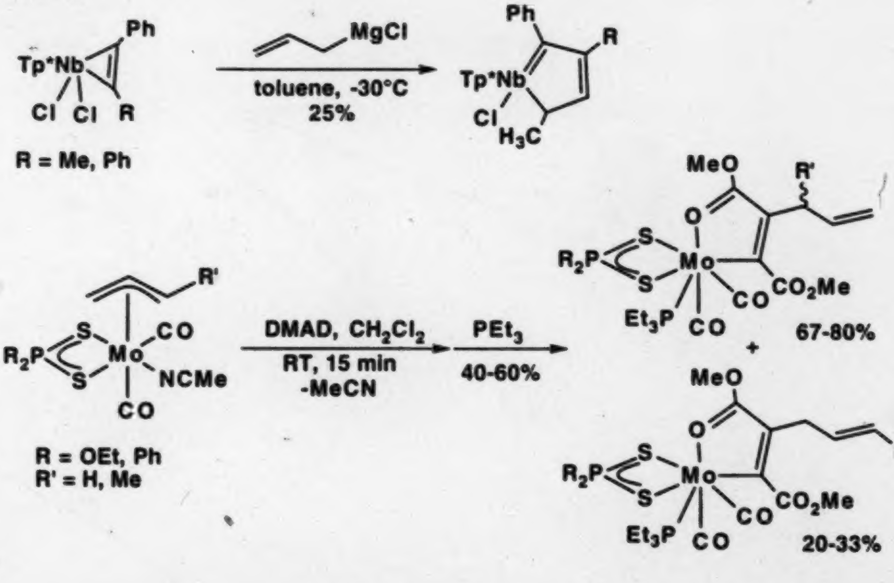
straightforward second insertion follows, generating the chelating vinyl diene complex **61**. Because no crystallographic analysis was undertaken, the *trans* assignment of $CF_3$ groups was based on spectroscopic data. Only one $CF_3$ group shows $J_{FH}$ coupling to the allyl fragment; furthermore, this group shows no F-F coupling, suggesting that the adjacent $CF_3$ group is in a *trans* orientation. The two $CF_3$ groups assigned to the $\alpha$ and $\beta$

carbon atoms show mutual coupling ($J_{FF}$ = 12 Hz) but no further splitting of the signals is observed.

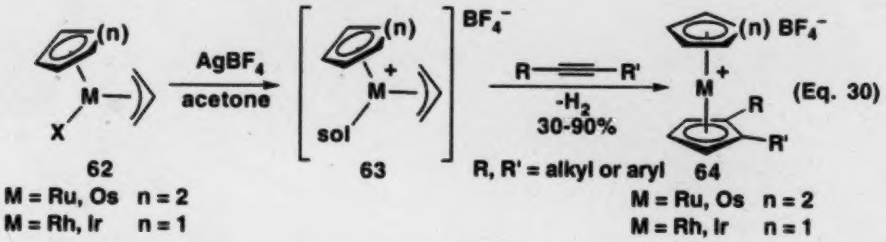
### *4. [3 + 2] Allyl/Alkyne Cycloaddition Reactions*

Allyl/alkyne coupling has been observed not only to form linear condensation products, but also to form cyclic complexes. The reaction of a tris(3,5-dimethylpyrazolyl)borate niobium alkyne complex with allyl magnesium chloride yields a rearranged niobacyclopentadiene product (Scheme **8**).[82a] A molybdenum allyl complex has been shown to react with DMAD to form an oxamolybdacyclopentadiene product (Scheme **8**).[82b] Both of these processes involve rather extensive rearrangements of the initial alkyne insertion product.

**Scheme 8**

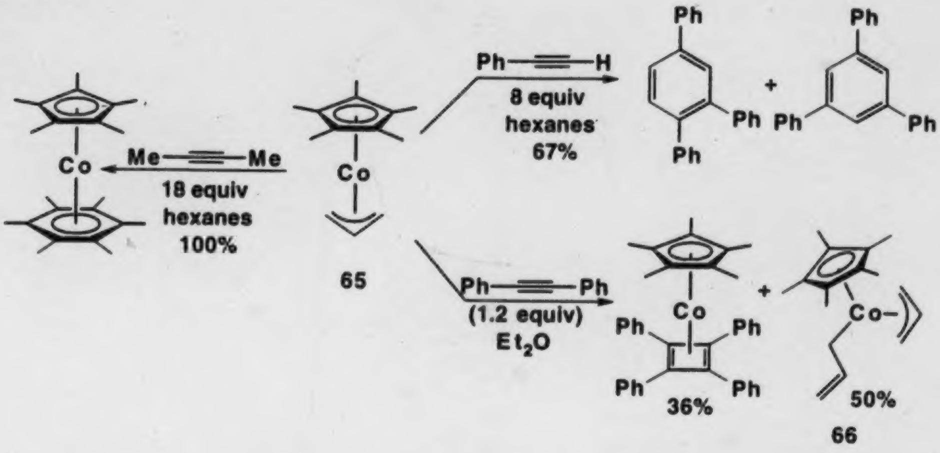

Tp*Nb
Ph
Cl
Cl
R
R = Me, Ph
MgCl
toluene, -30°C
25%
Tp*Nb
Ph
R
Cl
H₃C
R'
R₂P
S
S
Mo
CO
NCMe
CO
R = OEt, Ph
R' = H, Me
DMAD, CH₂Cl₂
RT, 15 min
-MeCN
PEt₃
40-60%
MeO
R'
O
Mo
CO
CO₂Me
Et₃P
CO
67-80%
+
MeO
O
R'
Mo
CO
CO₂Me
Et₃P
CO
20-33%

Another pattern of allyl/alkyne insertion is seen in the reaction of several Group 8 and 9 allyl complexes with alkynes: a [3 + 2] metal-mediated dehydrogenative cycloaddition. Rubezhov has provided numerous examples of such [3 + 2] allyl/alkyne cycloaddition reactions using allyl halide complexes **62** (Eq. **30**).[83] Unsaturated intermediates **63** are generated by a halide metathesis reaction with silver tetrafluoroborate and are presumed to coordinate and insert one equivalent of alkyne. Cyclization of the initial insertion product is followed by a loss of dihydrogen to form sandwich complexes **64** in generally good but variable yield (30-90%). In these reactions, the product of initial allyl/alkyne insertion may parallel the examples reported by Clark and Green; however, no mechanistic work is reported by Rubezhov. The presumed mechanism of this process along with additional supporting evidence will be discussed in later sections of this chapter.



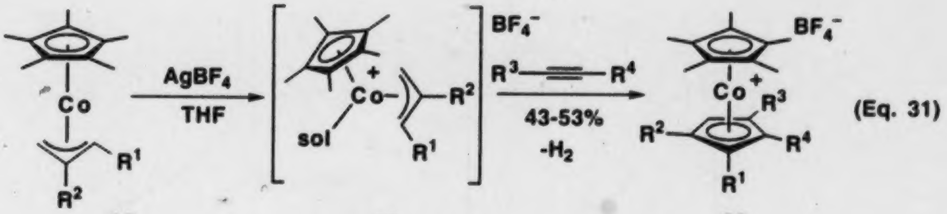
Recently, Nehl reported a similar [3 + 2] allyl/alkyne cycloaddition reactivity pattern using a cobalt template.[84] A large change in the reactivity pattern is noted with a change in the oxidation state of the cobalt (Scheme **9**). The reactions of pentamethylcyclopentadienylcobalt(II) allyl **65** with alkynes yield a variety of products arising from alkyne dimerization and trimerization, with no incorporation of the allyl ligand into the products (Scheme **9**). In the reaction with diphenylacetylene, however, ($\eta^5$-$C_5Me_5$)Co($\eta^1$-allyl)($\eta^3$-allyl) (**66**) is isolated in addition to a tetraphenylcyclobutadiene complex, but the fate of the allyl ligand in most other reactions is unknown. In some cases, the presence of uncomplexed benzenes (from cobalt-catalyzed alkyne trimerization) is detected by $^1$H NMR spectroscopy. Complex **65** is also known to co-cyclize alkynes and nitriles to form pyridine rings.[85]

**Scheme 9**



Co
Me—≡—Me
18 equiv
hexanes
100%
Co
65
Ph—≡—H
8 equiv
hexanes
67%
Ph
Ph
Ph
+
Ph
Ph
Ph
Ph—≡—Ph
(1.2 equiv)
Et₂O
Co
Ph
Ph
Ph
Ph
36%
+
Co
50%
66

Oxidation of **65** to the cobalt(III) allyl cation **67** results in dramatically different chemistry (Eq. **31**). The reaction of alkyne with the cobalt(III) system in tetrahydrofuran solvent yields sandwich compounds **68** similar to those observed by Rubezhov.

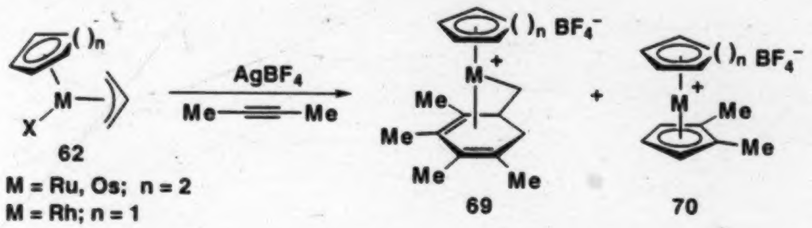


Co
R¹
R²
AgBF₄
THF
Co
sol
R²
R¹
BF₄⁻
R³—≡—R⁴
43-53%
-H₂
BF₄⁻
Co
R³
R²
R⁴
R¹
(Eq. 31)

**65** **67** **68**

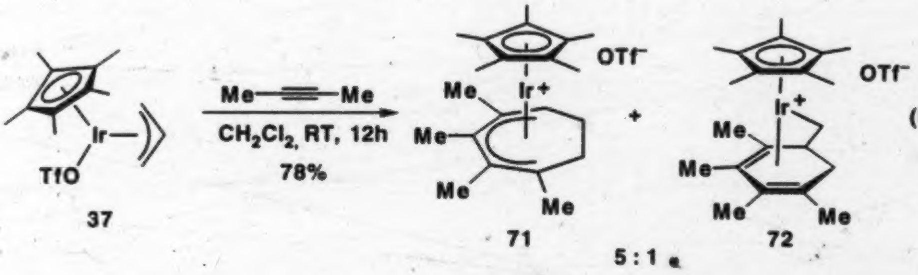
*5. [3 + 2 + 2] Allyl/Alkyne Cycloaddition Reactions*

Rubezhov has reported a rare case of double alkyne insertion into an allyl ligand using 2-butyne.[86] The formation of this unique 2:1 cycloadduct **69** proceeds smoothly in 32-49% yields using several metal templates, but this new reactivity pattern is limited to the use of 2-butyne (Eq. **32**). The proposed mechanism for the formation of these compounds will be discussed later in this chapter. In the reaction of ($\eta^6$-benzene)ruthenium($\eta^3$-allyl)$^+$ $BF_4^-$ with equimolar alkyne, Rubezhov reports a product mixture of 4:1 in favor of the methanocyclohexadiene complex **69** over the single insertion product, metallicenium complex **70**. Data for the product ratio with larger amounts of alkyne or with other metal templates is not reported.



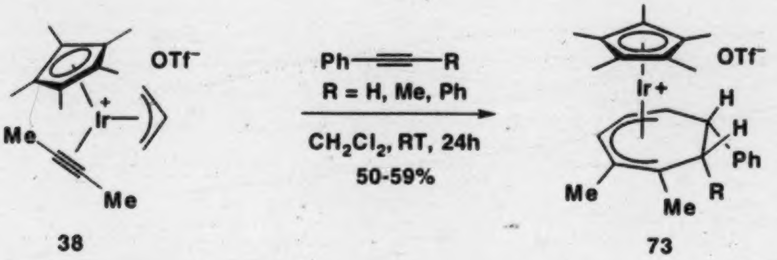
(Eq. 32)

On the basis of Rubezhov's results, it was thought that this reactivity pattern could be altered to produce seven-membered rings by using a different arrangement of ancillary ligands.[61] This selectivity for the reaction was accomplished by Schwiebert in this research group, who has shown that by using the more sterically demanding pentamethylcyclopentadienyl ligand, the reaction of **37** with excess 2-butyne gives a mixture of seven and six-membered ring systems **71** and **72** in a reasonably selective 5:1 ratio (Eq. **33**).[61]



(Eq. 33)

The greater stability imparted to the complexes by the electronic properties of the pentamethylcyclopentadienyl ligand also enabled Schwiebert to isolate a competent intermediate in the cyclization pathway. Addition of 2-butyne to the triflate complex **37** in benzene/diethyl ether forms an allyl/alkyne complex **38**, which precipitates from solution. Further reaction of this complex in dichloromethane with other alkynes yields one major product, the seven-membered ring complex **73** (Eq. 34), which presumably is formed through the same mechanism that produces **71**. Also seen in this reaction are varying amounts of isomeric seven-membered ring complexes (20-50% of the product mixture), which appear to be the result of a series of hydride shifts, isomerizing the main product **73**.

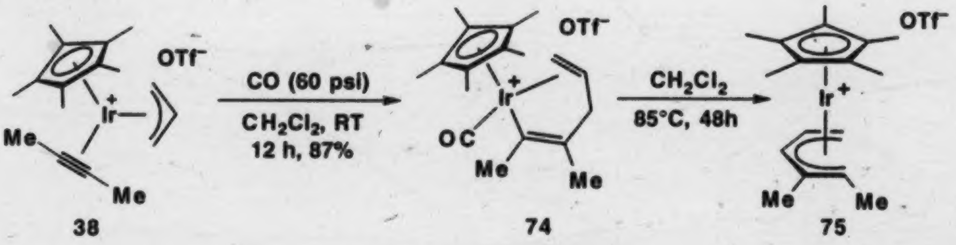


OTf⁻
Ir
Me
Me
38
Ph—≡—R
R = H, Me, Ph
CH₂Cl₂, RT, 24h
50-59%
OTf⁻
Ir+
H
H
Ph
R
Me
Me
73

(Eq. 34)

Additional evidence of the reaction pathway is obtained by trapping the direct product of allyl/alkyne insertion with carbon monoxide, although some $[(C_5Me_5)Ir(C_3H_5)(CO)]^+$ $OTf^-$ is formed from alkyne displacement by CO prior to allyl migration. The resulting vinyl carbonyl complex **74** is presumed to model the product of initial allyl/alkyne insertion, where CO takes the place of a more labile molecule, such as solvent or additional alkyne, in the actual [3 + 2 + 2] cycloaddition process (Scheme **10**). Interestingly, thermolysis of the vinyl carbonyl complex **74** results in the formation of a complex that was tentatively assigned as the 1,2-dimethylpentadienyl complex **75**,[62] in a process remarkably similar to the allyl/alkyne migratory insertion reactions reported by Hermann and Betz.[78] However, the spectroscopic data for complex **75** does not correspond well to other pentadienyl complexes, suggesting that a different structure is in fact formed.[87]

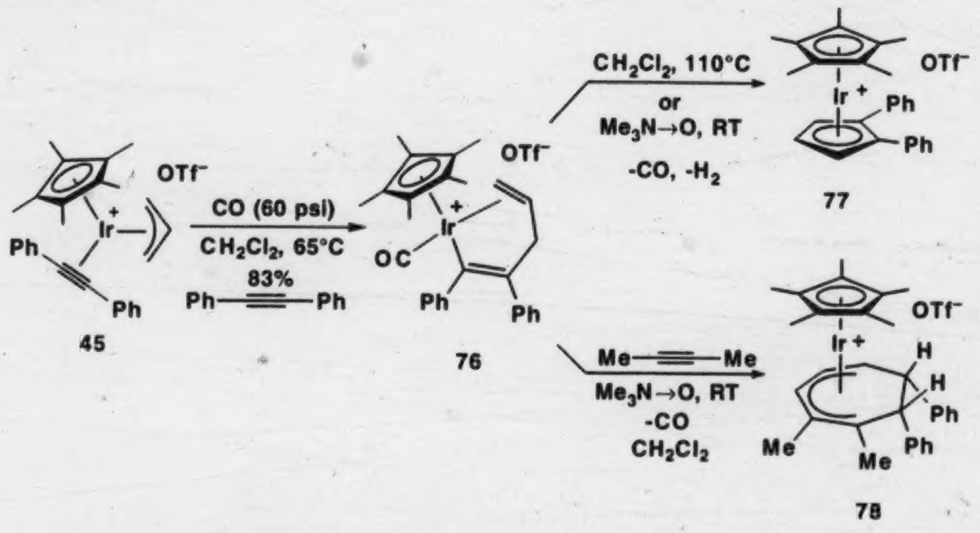
**Scheme 10**



OTf⁻
Ir
Me
Me
38
CO (60 psi)
CH₂Cl₂, RT
12 h, 87%
OTf⁻
Ir
OC
Me
Me
74
CH₂Cl₂
85°C, 48h
OTf⁻
Ir⁺
Me
Me
75

Other allyl/alkyne complexes can also be trapped at intermediate stages; the reactivity of diphenylacetylene complex **45**, formed under the same conditions as **38**, closely resembles that seen in both butyne complex **38** and in Rubezhov's work (Scheme **11**). Reaction under an atmosphere of CO also produces a vinyl carbonyl complex, **76**;

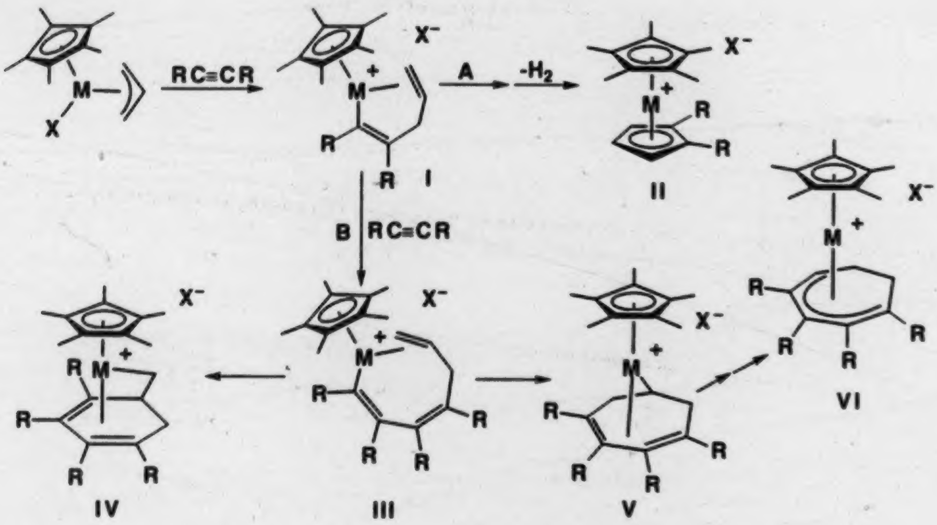
**Scheme 11**



however, a different reactivity pattern is subsequently seen. Rather than isomerization to form an acyclic pentadienyl complex, treatment of **76** with trimethylamine-N-oxide or thermolysis leads to the formation of cyclic 1,2-diphenylcyclopentadienyl complex **77**. The reaction of complex **76** with 2-butyne and trimethylamine-N-oxide, produces the seven-membered ring complex **78** previously observed in the direct reaction of **45** with 2-butyne (Eq. **34**). This implicates such vinyl olefin complexes as competent intermediates in the formation of seven-membered ring complexes. However, no evidence has been obtained for more advanced intermediate complexes in the [3 + 2 + 2] cycloaddition pathway.

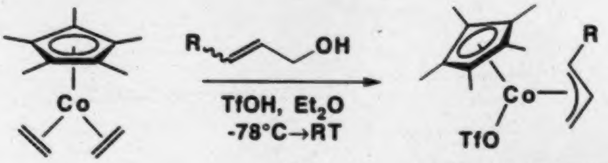
Based on these results, a working mechanistic rationale is presented for the formation of seven-membered ring systems in these [3 + 2 + 2] cycloaddition processes (Scheme **12**). Initial insertion of an alkyne molecule into the allyl ligand generates vinyl olefin intermediate **I**, which can be trapped by added ligand (*e.g.* **76**). However, intermediate **I** can also cyclize to five-membered ring **II** (Path **A**, Scheme **12**) or insert a second alkyne (Path **B**, Scheme **12**). The insertion of a second alkyne generates a vinyl diene intermediate **III**, which cyclizes to either a six-membered (**IV**) or seven-membered (**V**) ring $\eta^1,\eta^4$-carbocycle by migratory insertion. This non-conjugated seven-membered ring intermediate is evidently unstable and undergoes β-hydride elimination and hydride reinsertion reactions to form an $\eta^5$-cycloheptadienyl product (*e.g.*, **VI**), where the final position of the substituents (R) depends on undetermined factors. A more comprehensive discussion of the cycloaddition mechanism is presented at the end of this chapter.

**Scheme 12**



### *6. Cobalt [3 + 2 + 2] Allyl/Alkyne Cycloaddition Reactivity Patterns*

With the goal of a more general and economical template for similar [3 + 2 + 2] cycloaddition reactivity in mind, Etkin attempted to extend this [3 + 2 + 2] allyl/alkyne cycloaddition reactivity pattern by using cobalt allyl complexes.[88,89] Pentamethylcyclopentadienylcobalt(allyl) triflate complex **80** is easily synthesized in good yield from the bis(ethylene) complex **79**,[90] allyl alcohol and triflic acid (Eq. **35**).[91] Unlike related manganese systems, where substituted allyl complexes can be formed from substituted allylic alcohols,[92] this cobalt methodology appears to be limited solely to the unsubstituted allyl alcohol. Attempts to use other allylic alcohols in this procedure give mostly paramagnetic decomposition products; only with crotyl alcohol is a small (ca. 20%) amount of impure crotyl triflate **81** isolated.



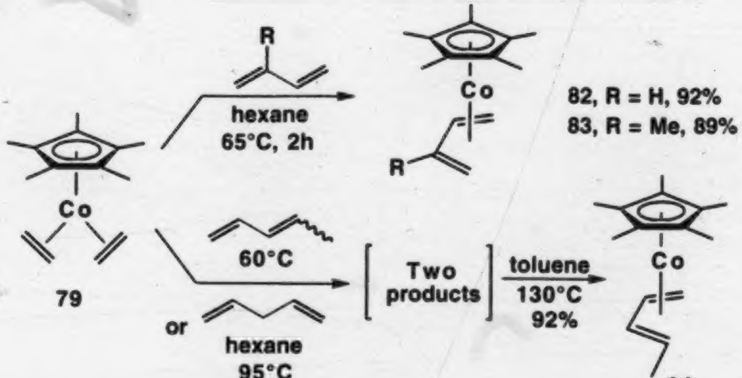
**79**

**80, R = H, quantitative**
**81, R = Me, ca. 20%**

(Eq. 35)

Due to the failure of the initial route to synthesize substituted allyl complexes, other simple methods were investigated. Although other procedures to generate (allyl)cobalt(halide) complexes are known in the literature,[93] the conversion of the halide to a triflate ligand by use of silver triflate was expected to be prohibitively difficult, based on the poor metathesis results obtained in the iridium systems.[61] The conversion of a diene ligand to an allyl complex by protonation is well established; thus, a facile synthesis of pentamethylcyclopentadienecobalt($\eta^4$-diene) complexes was sought. Exchange of the CO ligands in CpCo(CO)$_2$ with acyclic 1,3 or 1,4 dienes is known, but generally requires prolonged photolysis or harsh conditions.[94] The ligand exchange chemistry of (C$_5$Me$_5$)Co(CO)$_2$ is also poorly developed and requires harsh conditions; in contrast, the chemistry of the more substitutionally labile (C$_5$Me$_5$)Co(C$_2$H$_4$)$_2$ **79** is quite facile and well known.[95,96] Exchange of butadiene, isoprene, and other dienes with the ethylene ligands of **79** occurs under mild conditions, generating diene complexes **82-84** in high yield (Scheme **13**). Occasionally, higher temperatures are required to isomerize

**Scheme 13**

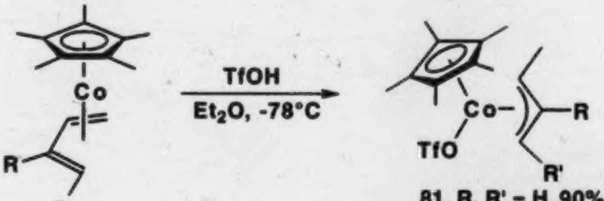


82, R = H, 92%
83, R = Me, 89%

84

mixtures of 1,3 and 1,4 diene complexes to a single isomer (*i.e.*, **84**) as seen in the exchange reaction of **79** with 1,4- and 1,3-pentadiene.[88]

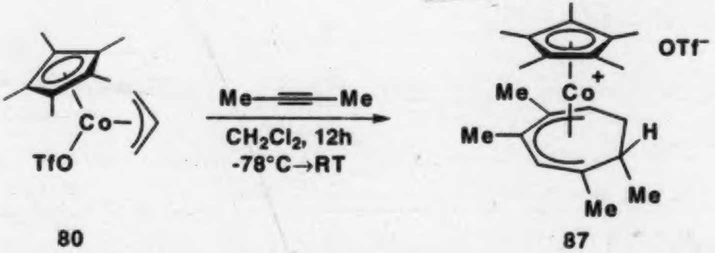
Cationic cobalt allyl complexes are easily formed from these readily available cobalt dienes complexes **82-84** by protonation using trifluoromethanesulfonic (triflic) acid. This transformation readily occurs in diethyl ether at -78°C to form crotyl, 1,2-dimethylallyl and 1,3-dimethylallyl complexes **81**, **85** and **86** as dark red-brown solids in high yield, although the formation of small amounts of a dark blue paramagnetic material is also noted (Eq. **36**).[88,89] This paramagnetic impurity can be removed by dissolution of the crude reaction product in small amounts of benzene and stirring the solution for several hours; this apparently allows time for the impurities to either decompose or aggregate. Filtration then removes the now insoluble impurities and recrystallization of the triflate complexes gives analytically pure compounds.



(Eq. 36)

81, R, R' = H, 90%
85, R, R' = Me, H, 80%
86, R, R' = H, Me, 82%

Although the reaction of the parent allyl triflate complex **80** with alkynes can yield seven-membered rings (*vide infra*), the crotyl complex **81** generates five-membered ring products almost exclusively when allowed to react with substituted alkynes. Even the unsubstituted allyl complex **80** forms these cyclopentadienyl compounds when allowed to react with bulky alkynes such as 4,4-dimethyl-2-pentyne, diphenylacetylene, or trimethylsilylacetylene in dichloromethane. More disappointing is the discovery that the allyl complex gives mixtures of isomeric seven-membered ring complexes when allowed to react with such unsymmetrical alkynes as propyne, 1-pentyne, and 1-phenylpropyne. Only two substituted alkynes, 2-butyne and 3,3-dimethyl-1-butyne, were observed to form single seven-membered ring adducts in good yield in the reaction with the allyl triflate complex **80** in dichloromethane. However, the product obtained from the reaction with 2-butyne (Eq. 37) is clearly a result of an extensive rearrangement, arising from a different, unprecedented mechanism, which will be discussed in a later chapter.



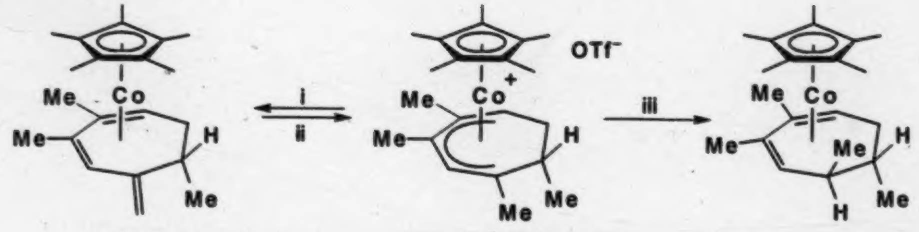
**80**

**87**

(Eq. 37)

The structure of complex **87** has been unambiguously established using extensive two-dimensional NMR spectroscopy. Further supporting evidence for this structure was obtained by the preparation of fully characterized derivatives such as the hydride adduct **88** (from addition of $LiEt_3BH$) and the deprotonation (NaH) product **89** (Scheme **14**).[88,89] A sequence of deprotonation and reprotonation steps was found to best effect the purification of complex **87**.[88,89]

Scheme 14

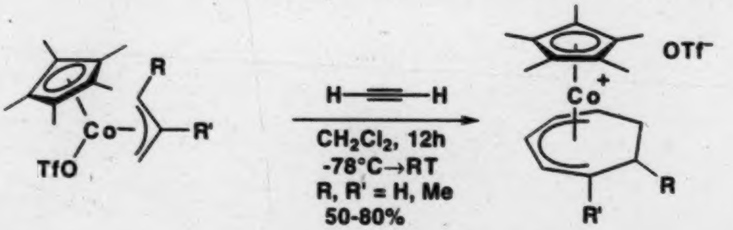


**88** **87** **89**

i) NaH, THF, 77%. ii) $HBF_4 \cdot Et_2O$, $Et_2O$, quant. iii) $Et_3BHLi$, THF, -78°C, 53%

The reaction of complex **80** with other alkynes such as phenylacetylene and cyclooctyne[97] appear to give single $\eta^5$-cycloheptadienyl complexes but the assignment of these products remained tentative, pending a more detailed examination. Strong solvent effects are noted in these reactions, which can dramatically alter the reactivity pattern. Reaction of the allyl complex **80** with alkyne (>1 equiv) in tetrahydrofuran rather than dichloromethane generates cobalticenium complexes exclusively, as also reported by Nehl.[84,85] Attempts to trap intermediates using CO are unsuccessful in cobalt, in contrast to the iridium system.[61,62] Furthermore, attempts to follow the reaction by $^1$H NMR spectroscopy also fail to show new intermediate complexes; only a compound tentatively assigned as the allyl/alkyne complex is seen.

It was found that complexes **80** (R, R' = H), **81** (R = Me, R' = H) and **85** (R, R' = Me) each undergo facile reaction with acetylene to form a single seven-membered ring isomer in high yield (Eq. **38**). Although only partially characterized by Etkin through the use of $^1$H NMR spectroscopy, the data strongly suggested that seven-membered ring complexes were present. A simple deuteration study undertaken using acetylene-$d_2$



(Eq. 38)

generated complex results that posed several mechanistic questions about rearrangements occurring in this system. Further discussion, as well as mechanistic proposals, will be presented in full in later sections.

### *C. Project Goals*

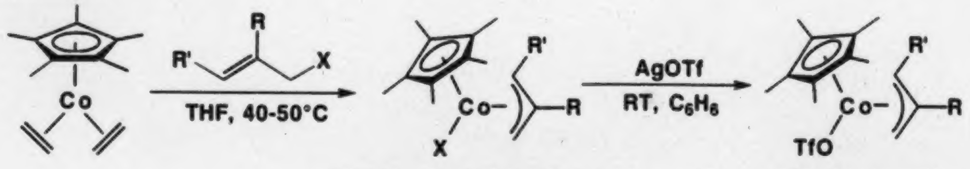
The pentamethylcyclopentadienylcobalt system produces some unexpected results with many reaction products not fully characterized. Our initial objective was to define the limits of the [3 + 2 + 2] chemistry in the pentamethylcyclopentadienyl cobalt system. In part, this requires further investigation into substituent effects on the allyl, as well as much greater development of the promising acetylene chemistry. As large steric barriers to the reactivity pathway appear to exist, we also endeavored to develop the cyclopentadienylcobalt system, a less sterically encumbered model, to test further [3 + 2 + 2] reactivity.

## II. Results and Discussion

### *A. Oxidative Synthesis of Other Allyl Complexes of Cobalt*

Although the preparation of various allyl complexes was established by Etkin, the procedure is limited by the availability of dienes. Some allyl complexes such as the cinnamyl, 2-methylallyl or carbomethoxyallyl complexes **90-92** cannot be prepared using such a sequence. They can, however, be readily synthesized using an oxidative addition procedure (Scheme **15**). Even the allyl and crotyl complexes **80** and **81** are easily made via this reactivity pattern. All of these cobalt allyl complexes have been tentatively assigned as having both an *exo* geometry ("point up") and *syn* substituent stereochemistry based on NOE measurements, $^1$H NMR coupling constants and comparison of the $^1$H spectrum with analogous iridium complexes.[62,88]

**Scheme 15**



79

90 R,R' = Me,H, X = Cl, 71%
91 R,R' = H,Ph, X = Cl, 70%
92 R,R' = H,$CO_2$Me, X = Br, 82%

93 R,R' = Me,H, 89%
94 R,R' = H,Ph, 76%

### *B. [3 + 2 + 2] Cycloaddition Reactions of Allyl Cobalt Complexes*

#### *1. General Discussion. Reaction Conditions and Product Characterization*

In contrast to the difficulty encountered using silver triflate as a halide abstracting agent in the iridium system, a reaction that requires excess silver triflate to proceed cleanly,[60,61,83] cobalt halides are replaced in good yield when allowed to react with one equivalent of silver triflate (Scheme **15**). Other reaction conditions may also be employed to generate unsaturated cobalt allyl complexes, such as the *in situ* reaction with silver salts used by Rubezhov.[83] This *in situ* ionization proceeds equally well using either silver tetrafluoroborate or silver triflate, although isolation of the ionized allyl complex has only been attempted with triflate as the counterion.

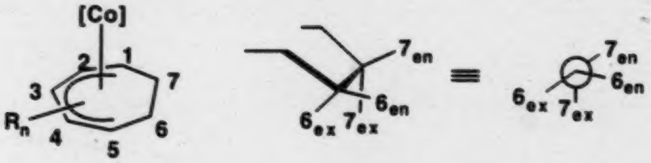
In order to avoid the use of expensive silver salts, other ionization methods were sought. It was thought that the use of a highly polar medium might preclude the need for an anion less coordinating than halide, thus 2,2,2-trifluoroethanol (TFE) was chosen in the hope that the cobalt halide would ionize solvolytically, forming a solvated outer sphere anion and leaving a more reactive cationic cobalt center. An added bonus is that the halide compounds are generally highly air and water stable, whereas the triflate complexes gradually decompose if exposed to air and water. Although this procedure works well for reactions with many alkynes, acetylene itself does not appear to react with the cobalt center in trifluoroethanol. Only extensive decomposition to uncharacterized blue paramagnetic material is observed upon addition of acetylene to a solution of cobalt allyl complex **80** in trifluoroethanol.

Other advances in technique have been made since Etkin's initial work, particularly in the isolation of [3 + 2 + 2] cycloadducts from various impurities. Most [3 + 2 + 2] cycloaddition reactions of pentamethylcyclopentadienyl cobalt allyl templates generate varying amounts of cobalticenium byproducts from [3 + 2] cycloaddition. As the solubility properties of these compounds are quite similar, they are often difficult to separate completely by crystallization, which hampers the identification and characterization of the products. It was discovered that both classes of compounds are stable to standard chromatographic conditions on the benchtop. Isolation and purification are normally accomplished through the use of flash chromatography on silica gel. The solvent polarity is varied depending on the difficulty of the separation but generally ranges from 4-7% methanol in dichloromethane. It should be noted that at least 1% methanol is required for any elution to occur. The cobalticenium products are much slower to elute and are often left on the column once the desired cycloheptadienyl compound is separated.

The assignments of the hydrogen atoms and substituent stereochemistry on the methylene carbons of the $\eta^5$-cycloheptadienyl products are based on careful comparison between $^1$H NMR spectroscopic data and dihedral angles obtained from the X-ray crystal structure of bicyclo[5.3.0]deca-1,3-dien-1-yl cobalt complex **111** (*vide infra*, p 63). An estimate of the coupling constant can be made from the dihedral angles using Karplus correlations.[98] However, the solution structure may differ or undergo rotational motions. The crystal structure determination also helps assign the substituent stereochemistry in other, similar, complexes as well, based on similarities of the spectroscopic data.

Several patterns in the $^1$H NMR spectra of cycloheptadienyl cobalt compounds are evident and can be used for preliminary structural assignments (Fig. 3). In cases where the ligand is symmetrical, either the unsubstituted seven-membered ring or a single substituent in the 3-position, only the hydrogen in the 3-position (if applicable) is unique. Although the $H_{1/5}$ and $H_{2/4}$ pairs appear to have first order patterns, the $H_{6exo}$ and $H_{7exo}$ atoms are magnetically inequivalent, as are the two $H_{endo}$ atoms; both are second order multiplets. Once the seven-membered ring is unsymmetrically substituted, all hydrogen atoms are rendered inequivalent; thus the remainder of this discussion applies only to the substituted ligands. The furthest downfield signal, typically about δ 7.2-6.3, can readily be assigned to the hydrogen attached to the central position of the pentadienyl framework. Other hydrogen atoms on the coordinated dienyl fragment resonate in the range of 4-6 ppm, with the two ends ($H_1$ and $H_5$) typically showing more shielding than the interior positions. The coupling constants for vicinal protons on the pentadienyl framework are almost always 7-9 Hz. However, there is a marked geometric difference between the two ends of the pentadienyl, as shown by the $J_{1\text{-}7}$ and $J_{5\text{-}6}$ values. While the $J_{5\text{-}6endo}$ and $J_{5\text{-}6exo}$ values are very different ($J$ = 8-9 and 4-6 Hz, respectively), there is little difference in the value of $J_{1\text{-}7endo}$ and $J_{1\text{-}7exo}$, a clear indication that the methylene carbons are generally in different relative spatial orientations. Note that in order to view these profoundly different values in the coupling constants, the conformational geometry must be fixed or, at the very least, changes must be slow on the NMR spectroscopy time scale. No further analysis (*e.g.*, variable temperature $^1$H NMR spectroscopy) was undertaken.

**Figure 3.** Numbering Scheme and Conformation of η$^5$-Cycloheptadienyl Complexes



The protons of the two adjacent methylene carbons also show characteristic chemical shift and coupling patterns. One signal resonates at particularly high field (δ 0.9 to -0.2) and has been defined as the $H_{6exo}$ proton. The consistent labeling of this high field resonance as $H_6$ helps simplify the tabulation of data and, although initially intended to agree with the nomenclature rule stipulating substituents be labeled with the smallest number possible, does not always lead to formally "correct" numbering schemes. The *exo* assignment for the upfield resonance is supported by Pauson's assignments of *endo* and *exo* substituents in cycloalkadienyl metal complexes.[100a] Pauson observed the general trend that the *endo* proton is found at lower field than the *exo* proton on the noncoordinated methylene carbon of $\eta^5$-cyclohexadienyl complexes, although this generalization appears to be valid only for first row metals.[100b] Crystallographic analysis of bicyclo[5.4.0]undecadienyl complex **111** (*vide infra*) indicates that the *exo* proton in this cobalt cycloheptadienyl complex is situated almost directly underneath the pentadienyl fragment, which is capable of generating an anisotropic effect, thus affecting the chemical shift. Similar situations are seen in the commonly cited example of ring currents in aromatic and annulene systems, where protons located above or below the central portions of the ring experience strong shielding effects. Thus, any proton situated immediately above or below the pentadienyl system should experience some degree of shielding, analogous to the more familiar example of the strong shielding of the inner protons in annulene systems.

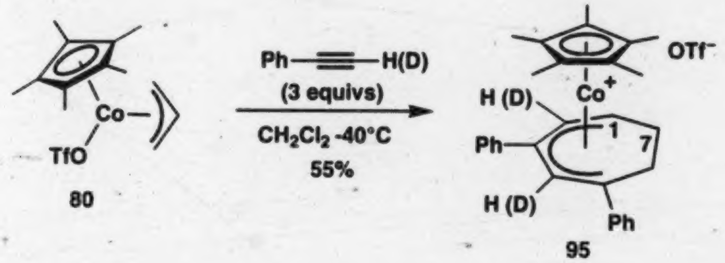
One other methylene hydrogen exhibits a characteristic pattern. The $H_{7endo}$ proton is shifted quite far downfield relative to the other methylene signals, to δ 2.5-3.5 in the $^1H$ NMR spectrum. Aside from chemical shift data, the coupling constants for this signal display fairly consistent values, resulting in a diagnostic spin coupling pattern: a resolved dddd multiplicity pattern, with coupling constants of approximately 16, 12, 8, and 4 Hz.

Because the final two protons ($H_{7exo}$ and $H_{6endo}$) of the methylene carbons are often multiplets or obscured by methyl group signals, few generalizations can be made. However, the conformation of the ring appears to be fairly rigid, which is reflected in the relatively constant magnitudes of various coupling constants. For example, the value of the vicinal coupling constants $J_{6endo\text{-}7exo}$ and $J_{6exo\text{-}7endo}$ are typically 0-3 and 9-13 Hz, respectively. The values for $J_{6endo\text{-}7endo}$ and $J_{6exo\text{-}7exo}$ are generally 7-9 and 3-6 Hz, respectively. The small value observed for $J_{6endo\text{-}7exo}$ is significant, suggesting an angle close to 90° between these two atoms. These data further support a static conformation (Figure **3**).

Once unambiguously assigned using heteronuclear correlated spectroscopy, the $^{13}C$ NMR spectrum also shows a significant number of characteristic patterns, both in the chemical shift and the value of the one bond C-H coupling constant ($^{1}J_{CH}$), which is dependent on its position in the ring. The $C_3$ carbon (Figure **3**) is normally the most deshielded signal; the $C_{2/4}$ and $C_{1/5}$ signals resonate further upfield, although there is a wide range of chemical shifts for these carbons and sometimes the signals are too close together to readily assign solely on the basis of the chemical shift. The value of $^{1}J_{CH}$ is also fairly diagnostic. Although this value is roughly the same for the $C_3$ and $C_{2/4}$ carbons, about 165-175 Hz and 163-168 Hz, respectively, the $C_{1/5}$ carbon atoms have a significantly smaller $^{1}J_{CH}$ value of 150-155 Hz. Thus, the terminal positions of the pentadienyl portion of the ring are quite evident in the coupled $^{13}C$ NMR spectrum. The $^{1}J_{CH}$ values for the methylene carbons, $C_6$ and $C_7$, show little variation from 125 Hz: the typical value for $sp^3$ hybridized carbon atoms. The $C_6$ carbon atom generally is observed at 30-40 ppm, while the $C_7$ resonates slightly downfield at 40-50 ppm.

### 2. *[3 + 2 + 2] Terminal Alkyne/Allyl Cycloaddition Reactions*

The reaction of terminal alkynes with the allyl template **80** produces the desired seven-membered ring systems, as both phenylacetylene and 3,3-dimethyl-1-butyne give good yields of seven-membered ring products when allowed to react in excess with complex **80** at -78°C in $CH_2Cl_2$. The dark red 3,5-diphenylcycloheptadienyl complex **95** can be isolated as an analytically pure microcrystalline powder in moderate yield, but only after repeated chromatography. This reaction also produces significant amounts of a brown uncharacterizable material that interferes with the product isolation and thus lowers the isolated yield. It was found that changing the reaction conditions to use slightly higher temperatures and a smaller excess of phenylacetylene gives better yields of cycloheptadienyl complex **95**, either from an inherently higher yield or simply from lower losses in isolation (Eq. **39**).



(Eq. 39)

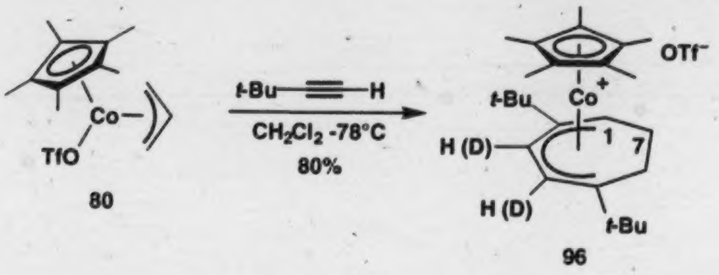
The $^1H$ NMR spectrum of **95** reveals only three downfield signals, consistent with both phenyl groups located on the coordinated pentadienyl portion of the ring. Furthermore, a sharp singlet at $\delta$ 6.47 ($H_4$) is observed, unusually far downfield for an $H_4$ position, attributed to an anisotropic effect of the phenyl substituents and indicating either a 1,3- or a 2,4-substitution pattern. Other downfield signals are found at 5.10 (d, $J_{2\text{-}1}$ = 9.4 Hz, $H_2$) and 4.74 (dddd, $H_1$) ppm: the vicinal AX pattern eliminates the possibility of 2,4-substitution pattern. The $H_1$ signal is shown by both homonuclear decoupling and two-dimensional techniques to be coupled to signals at $\delta$ 3.24 ($H_{7endo}$), $\delta$ 2.69 ($H_{7exo}$)

and δ 2.04 ($H_{6endo}$); all coupling constants, however, are quite small (2-3 Hz). As the hydrogen atoms that resonate at δ 3.24 ($H_{7endo}$) and δ 2.69 ($H_{7exo}$) show a mutual large (17 Hz) coupling, they are likely to be geminal and are assigned to the $H_7$ position adjacent to $H_1$. The second methylene unit is indicated by a large coupling constant of 13 Hz between δ 2.04 ($H_{6endo}$) and δ 0.58 ($H_{6exo}$). Although the $J_{6exo\text{-}7endo}$ coupling constant is also large (12.2 Hz), the other $J$ values are smaller (4-7 Hz). Data from the gated decoupled $^{13}C$ NMR spectrum also support the 1,3-disubstituted dienyl structure. Three carbon signals (δ 91.8, 87.9, and 86.0), assigned to $C_4$, $C_2$ and $C_1$, respectively, are doublets in the gated spectrum, with $^1J_{CH}$ values of 145-163 Hz, indicative of near-$sp^2$ hybridization. Two other singlets are observed downfield at δ 114.5 ($C_3$) and δ 107.9 ($C_5$), consistent with coordinated quaternary $sp^2$ hybridized carbon atoms. The methylene carbons are assigned to the triplet ($^1J_{CH}$ = 132-133 Hz) signals at 46.2 ($C_7$) and 32.3 ($C_6$) ppm.

A simple deuterium labeling study was undertaken, by preparing phenylacetylene-$d_1$ from lithiophenylacetylene and $D_2O$ and allowing a slight excess of the deuterated alkyne to react with triflate complex **80**. The alkyne D(H) atoms are located exclusively adjacent to each phenyl ring, indicating that there is no rearrangement of the alkyne substituents.

In contrast, the dark green di-*t*-butyl complex **96**, formed from the reaction of **80** with 3,3-dimethyl-1-butyne, is isolated in high yield after direct crystallization of the crude reaction product from $CH_2Cl_2/Et_2O$ (Eq. **40**).[88,89] The bulky *t*-butyl groups must perturb the coordination geometry, as reflected by the color of the compound, but no further structural investigation was undertaken, due to a difficulty in obtaining X-ray quality crystalline material. An analytically pure dark green powder can also be obtained after flash chromatography. The $^1H$ NMR spectrum exhibits an isolated AX system, with doublets at δ 7.41 and δ 5.40 for $H_3$ and $H_4$, respectively, consistent with 1,4 substitution.

The greater downfield shift of these hydrogen atoms is presumably another indication of perturbed coordination. When the allyl triflate complex **80** is allowed to react with



(Eq. 40)

terminally deuterated *t*-butylacetylene-$d_1$, the deuterium labels are found adjacent to one another and flanked by the *t*-butyl groups. Some degree of commonality in the spectral properties of structures **95** and **96** can be seen (Table **1**), despite the rather different substitution patterns. In particular, the 6-*exo* and 7-*endo* protons have highly consistent chemical shifts and multiplicity patterns.

According to the proposed mechanism, these two complexes must arise from different alkyne insertion orientations (Scheme **16**). The diphenyl complex **95** is formed from a head-to-tail insertion process, with each insertion placing the phenyl group away from the metal center (**I**, Scheme **16**). In the absence of further data, it is equally likely that the insertion places the phenyl group adjacent to the metal (**II**, Scheme **16**), as cyclization of both intermediates provides the same enantiomeric σ-diene structure (**III**, Scheme **16**). Both structures **I** and **II** are nominally 16-electron, coordinatively unsaturated intermediates. However, these intermediates are likely stabilized by the coordination of a solvent molecule, a triflate counterion, or the free double bond in the ligand.

Arguments can be made for either insertion regioisomer. The first structure shown (**I**, Scheme **16**) is expected to have greater electron delocalization by placing the phenyl ring at the end of the diene group. The steric presence of the phenyl groups may also be minimized in structure **I**, as they are placed away from the metal. Structure **II** in

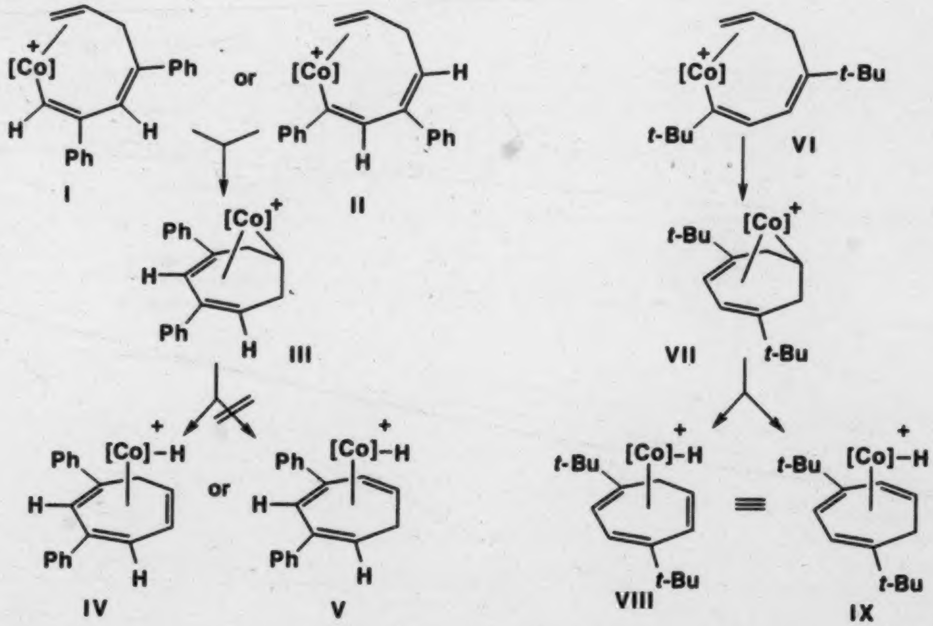
**Table 1.** Comparative $^1$H NMR Spectroscopic Data for Cp* Cycloheptadienyl Complexes

| | **95** | **96** | **97** | **98** |
|---|---|---|---|---|
| **$H_1$**<br>$J_{1\text{-}2}$ | 4.73 (m)<br>9.1 Hz | 4.79 (dd)<br>b | 4.30 (s)<br>b | 4.20 (br s)<br>b |
| **$H_2$**<br>$J_{2\text{-}3}$ | 5.10 (d)<br>b | b | b | b |
| **$H_3$**<br>$J_{3\text{-}4}$ | b | 7.41 (d)<br>6 Hz | b | b |
| **$H_4$**<br>$J_{4\text{-}5}$ | 6.47 (s)<br>b | 5.40 (dt)[c]<br>b | b | 5.79 (s)<br>b |
| **$H_5$**<br>$J_{5\text{-}6endo}$<br>$J_{5\text{-}6exo}$ | b | b | b | b |
| **$H_{6endo}$**<br>$J_{6endo\text{-}6exo}$<br>$J_{6endo\text{-}7endo}$<br>$J_{6endo\text{-}7exo}$ | 2.04 (ddd)<br>13 Hz<br>6.9 Hz<br>4.1 Hz | 1.80 (m)<br>12 Hz<br>a<br>3.6 Hz | 1.50 (m)<br>12.2 Hz<br>a<br>a | 1.95 (m)<br>12.6 Hz<br>7.0 Hz<br>3.7 Hz |
| **$H_{6exo}$**<br>$J_{6exo\text{-}7endo}$<br>$J_{6exo\text{-}7exo}$ | 0.58 (ddd)<br>13 Hz<br>4.5 Hz | -0.19 (ddd)<br>12 Hz<br>3 Hz | -0.06 (ddd)<br>12.2 Hz<br>4.8 Hz | 0.35 (ddd)<br>12.6 Hz<br>4.3 Hz |
| **$H_{7endo}$**<br>$J_{7endo\text{-}7exo}$<br>$J_{7endo\text{-}1}$ | 3.24 (dddd)<br>16.9 Hz<br>2.4 Hz | 3.24 (dddd)<br>17 Hz<br>1.4 Hz | 2.95 (m)<br>16 Hz<br>a | 3.16 (dddd)<br>16 Hz<br>3.0 Hz |
| **$H_{7exo}$**<br>$J_{7exo\text{-}1}$ | 2.69 (dddd)<br>4 Hz | 2.98 (dddd)<br>6 Hz | 2.35 (dt)<br>small | 2.59 (ddd)<br>3.7 Hz |

[a] Numerical value for the coupling constant was not obtained due to second order character or complexity of the signal. [b] Not applicable due to a non- hydrogen substituent. [c] Additional splitting observed due to long range coupling.

Scheme **16**, although perhaps marginally more sterically crowded, is favored by a different electronic argument. Normally, α-substituents are unfavorable, unless the substituent is a strongly electron withdrawing group; thus, the α-phenyl group may provide some stabilization to the metal-carbon bond. Additionally, the observed structure for compound **98** (*vide infra*) can only arise if the phenyl group of the phenylacetylene is placed adjacent to the metal. This would seem to indicate that the insertion geometry is not controlled by steric effects; although this cannot be stated conclusively, since the cyclooctene ring in the transition state forming **98** has much different steric effects than the lone phenyl group in **95**. Furthermore, this is to some extent irrelevant in the present example, as the cyclization process converts both regioisomers into the same $\eta^1,\eta^4$-σ-diene intermediate (**III**).

**Scheme 16**

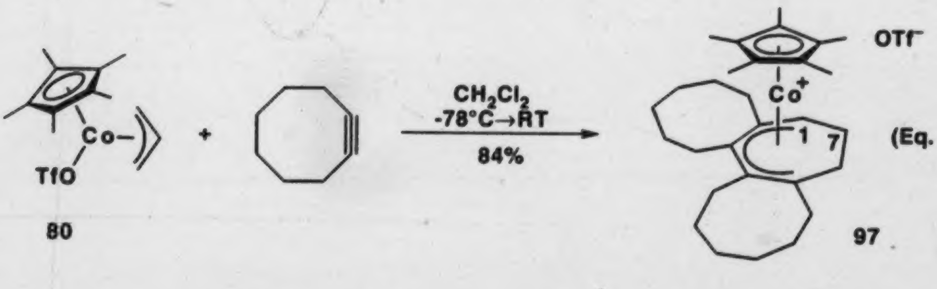


The σ-diene intermediate (**III**, Scheme **16**) can in theory undergo β-hydride elimination on either side, generating two possible triene hydride intermediates (**IV** and **V**). However, as only one isomer of the cycloheptadienyl product is observed, some barriers must exist to prevent re-insertion of the hydride into the triene ligand. Delivery of the hydride directly on top of a substituent, while seen in the Schwiebert iridium system,[61,62] is not observed in these cobalt complexes, suggesting a possible steric barrier, perhaps arising from the greater distance from the metal to substituted positions. Diphenylcycloheptadienyl complex **95** has one phenyl substituent at the end of the pentadienyl frame, suggesting that this isomer may be favored because of additional stabilization provide by electron delocalization into the phenyl ring. Other data from the deuteration experiment suggest that intermediate **V** is disfavored; the observed deuteration pattern cannot be obtained directly by hydride reinsertion in this regioisomer.

In contrast, di-*t*-butylcycloheptadienyl complex **96** can only be formed by a specific alkyne insertion pathway: a tail-to-tail alkyne insertion pattern (**VI**, Scheme **16**). The initial insertion of *t*-butylacetylene places the large *t*-butyl group away from the metal. Subsequent insertion of the second alkyne places the large group near to the metal, perhaps in order to minimize the steric interaction between the bulky *t*-butyl groups. The unusual insertion regioselectivity can also be explained by a fundamentally different mechanism proposed to operate in the anomalous reaction of allyl complex **80** with 2-butyne (Eq. **37**); this will be discussed later. Cyclization to intermediate (**VII**) is followed by β-hydride elimination to either side, producing enantiomeric intermediates (**VIII**) and (**IX**). However, as noted for the phenyl substituted complex, hydride re-insertion to a substituted position appears to be disfavored, and the hydride is reinserted only into the unsubstituted end of the pentadienyl framework, resulting in the observed cycloheptadienyl complex **96**.

Although these alkynes provide a single cycloheptadienyl product, it is important to note that with unsymmetric alkynes, the possibility of multiple isomers exists. Unsymmetric alkynes with smaller alkyl groups, such as propyne, do in fact produce inseparable mixtures of isomeric cycloheptadienyl complexes.[87] Thus, this [3 + 2 + 2] cycloaddition reactivity pathway is not likely to successfully produce single compounds using unsymmetric alkynes with small variations in the alkyne substituents, *i.e.*, other terminal n-alkynes. The above examples are unusual in that a strong steric or electronic effect is present, which favors the formation of a single $\eta^5$-cycloheptadienyl isomer.

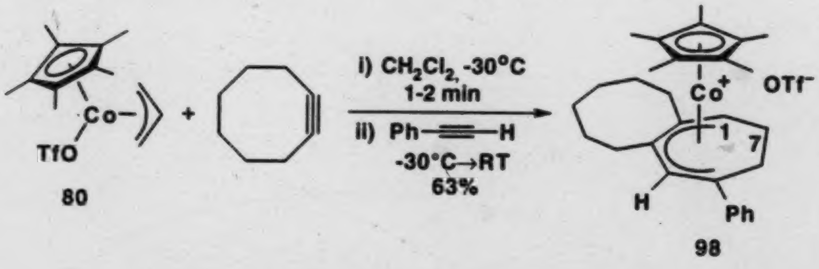
The highly reactive strained-ring cyclooctyne[97] gives an isolable $\eta^5$-cycloheptadienyl complex **97** when allowed to react with allyl complex **80** (Eq. **41**). The cyclooctyne bis-adduct **97** appears to be a straightforward example of the [3 + 2 + 2] pathway, in contrast to the unexpected results obtained with 2-butyne. Spectral data are consistent with a 1,2,3,4-tetrasubstituted $\eta^5$-cycloheptadienyl complex, although several details are obscured by the methylene envelope produced by the cyclooctyne -$CH_2$- units. In such systems, the gated decoupled $^{13}C$ NMR spectrum is often more informative than the $^1H$ NMR spectrum. There are four singlets in the gated decoupled $^{13}C$ NMR spectrum at 119.1, 111.2, 107.3 and 105.7 ppm, assigned to the four substituted carbons of the pentadienyl framework of **97**. An additional doublet ($J$ = 149.4) at $\delta$ 83.9 is consistent with the remaining carbon ($C_1$). Using heteronuclear correlated spectroscopy, this latter signal is seen to correlate with the $\delta$ 4.30 ($H_1$) signal in the $^1H$ NMR spectrum, which is a further indication that the seven-membered ring has a tetrasubstituted pentadienyl fragment.



(Eq. 41)

It was expected that the strong dative bond formed between cyclooctyne and the cobalt center would allow a different alkyne to be used for the second insertion. Cyclooctyne should experience a significant amount of rehybridization toward $sp^2$ character upon coordination to a metal center, thereby relieving the strain associated with a triple bond in a relatively small ring system. Decoordination of this alkyne would re-establish the strain energy, thus alkyne dissociation should be disfavored and the presence of a second alkyne in solution should not have adverse effects. This procedure may thus allow the formation of interesting mixed alkyne complexes. The possibility of the *in situ* generation of smaller cycloalkynes or benzyne to form a wide variety of these mixed alkyne products should not be ignored.

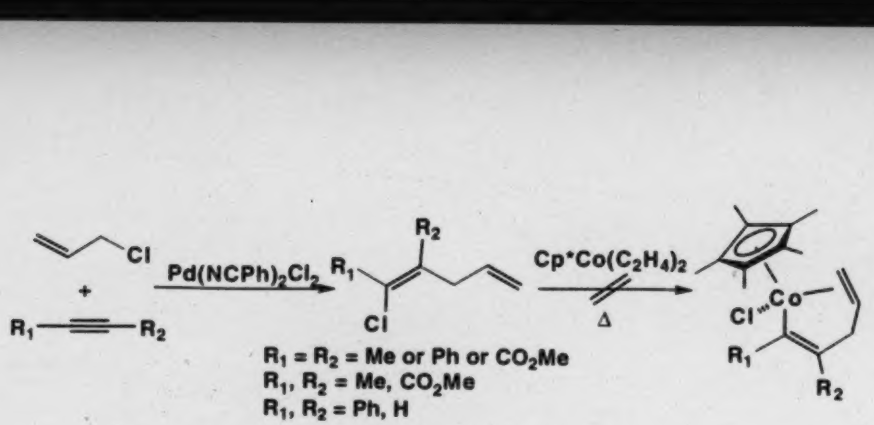
The addition of phenylacetylene (3 equivalents) to a solution of cyclooctyne and complex **80** in dichloromethane at low (-78°C) temperature, followed by slowly warming the reaction mixture to room temperature yields the mixed adduct **98** (Eq. **42**) in high yield. The structure of **98** is suggested by signals in the $^1$H NMR spectrum at δ 5.79 and 4.20 for the $H_4$ and $H_1$ protons, respectively. These two signals are the only deshielded signals other than phenyl resonances. The $^{13}$C NMR spectrum also supports the assignment of a trisubstituted ring, as evidenced by the two doublets in the gated decoupled $^{13}$C spectrum at δ 90.9 ($J$ = 163 Hz) and δ 82.4 ($J$ = 162 Hz), attributed to the unsubstituted coordinated sp$^2$ carbons, $C_4$ and $C_1$. Further, $^1$H-$^{13}$C correlated spectroscopy (HETCORR) indicates that these carbons are attached to the protons resonating at δ 5.79 and 4.20. Only two of the three quaternary carbon signals of the pentadienyl fragment are conclusively identified; it is likely that the third signal is obscured by one of the phenyl carbon resonances.



(Eq. 42)

Only one such example of such mixed alkyne cycloaddition was obtained due to a certain degree of difficulty inherent in the procedure. The second alkyne must be added after the initial irreversible coordination or insertion has happened, but before the cyclization to a five-membered ring can occur. Although this reactivity strongly parallels that seen in Schwiebert's iridium system,[61,62] the cobalt reaction is much more difficult to control. Repeated attempts to isolate similar allyl/alkyne complexes analogous to iridium complexes **38** or **45** failed to yield tractable material. The sequential addition technique for the production of mixed alkyne products such as cycloheptadienyl complex **98** appears to work only in this specific example. Attempts to repeat this reaction using alkynes other than cyclooctyne generally returned uncontrolled mixtures of [3 + 2 + 2] cycloadducts from only one alkyne; mixed alkyne products were not generally observed. This is evidence for strong cyclooctyne coordination; the results with other alkynes are consistent with a reversible alkyne coordination.

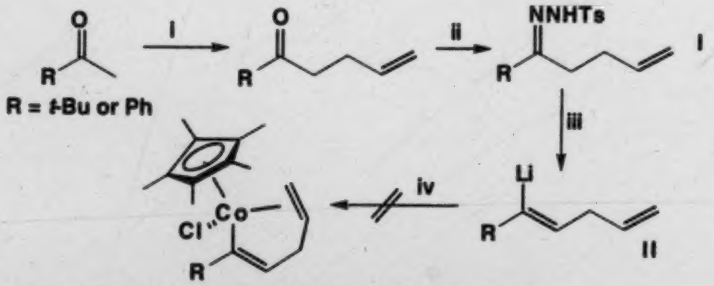
Given the failure of two different alkynes to produce mixed-alkyne products in a [3 + 2 + 2] cycloaddition reaction, attempts were made to circumvent this process. If an intact vinyl alkene moiety could be independently synthesized and attached to the cobalt center, addition of alkyne should produce the same cycloheptadienyl products as one would expect from a controlled cycloaddition with two different alkynes. Thus, 1-chloro-1,4-pentadienes were synthesized using the procedure of Kaneda (Eq. **43**).[101] This approach has additional potential value, since it allows for greater functionality in the final product, while avoiding difficulties encountered in coordinating strongly electronically perturbed alkynes. However, the attempted thermal oxidative addition of these vinyl halides to $(\eta^5\text{-}C_5Me_5)Co(C_2H_4)_2$ does not proceed cleanly and tractable products could not be obtained from these reactions. The oxidative addition of dichloromethane to $(\eta^5\text{-}C_5Me_5)Co(CO)_2$ has been shown to proceed under extended (8-12 h) photolysis.[95e] This procedure may prove more effective for the oxidative addition of vinyl halides but it has yet to be investigated in this series.


Cl
+
$R_1$
$R_2$
$Pd(NCPh)_2Cl_2$
$R_1$
$R_2$
Cl
$R_1 = R_2$ = Me or Ph or $CO_2Me$
$R_1$, $R_2$ = Me, $CO_2Me$
$R_1$, $R_2$ = Ph, H
$Cp^*Co(C_2H_4)_2$
Δ
Cl
Co
$R_1$
$R_2$

(Eq. 43)

One similar process also fails to yield tractable material. Allylation of the sodium enolate of pinacolone or acetophenone yields unsaturated ketones (Scheme **17**). Conversion to the tosyl hydrazone **I** and reduction with BuLi are known to form vinyllithium intermediates such as **II**.[102] Unfortunately, the reaction of [($\eta^5$-$C_5Me_5$)$CoCl_2$]$_2$[103] with *in situ* formed vinyllithium (**II**) fails to yield tractable material. The reaction of pentadienylpotassium[104] (prepared from 1,3 pentadiene, BuLi and KO-*t*-Bu) with ($\eta^5$-$C_5Me_5$)$CoI_2$(CO)[105] also fails to yield tractable material. Quite likely, the reaction with the vinyllithium results in a one electron reduction of the cobalt complex, rather than a metathesis reaction with a halide ligand. However, the reaction of pentadienylpotassium with the lower valent [($\eta^5$-$C_5Me_5$)CoCl]$_2$,[106] followed by oxidation, also fails to give the expected ($\eta^5$-$C_5Me_5$)Co ($\eta^5$-pentadienyl) cation, or any other tractable material.

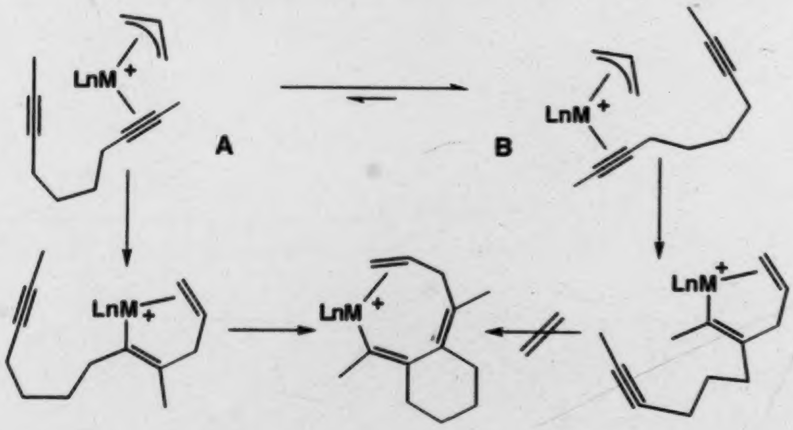
**Scheme 17**


O
R
R = t-Bu or Ph
i
O
R
ii
NNHTs
R
I
iii
Li
R
II
iv
Co
Cl
R

i) NaH, allyl bromide, THF, -78°C. ii) $NH_2NHTs$, EtOH, reflux.
iii) BuLi, THF, RT. iv) [$Cp^*CoCl_2$]$_2$, THF, -78°C.

Other reactivity patterns observed in the iridium template **37** are also not obtained using the cobalt systems. Allowing α,ω-diynes to react with allyl complex **80**, in an attempt to form bicyclic ring systems similar to the known iridium reactivity pattern, does not produce cobalt cycloheptadienyl complexes analogous to bicyclic complex **40** (Eq. **20**, page 17). Most terminal diynes (such as 1,7-heptadiyne) again fail to give tractable material leading to a variety of products by TLC analysis. The disubstituted diyne, 2,8-octadiyne, gives a similar result. It is unclear why these results should differ so much from the reactivity of the iridium series. However, in order to produce the desired bicyclic complex, the first allyl/alkyne insertion must occur with regioselectivity such that the tethered alkyne is terminal and can reach the metal center (**A**, Figure **4**). It may be that the alkyne coordination to iridium is reversible, allowing time for this correct insertion geometry to be established prior to the irreversible migration. The more reactive cobalt center may quickly coordinate and kinetically insert the alkyne, even if the geometry is wrong for cyclization (**B** in Figure **4**). As seen in path **B**, the tethered alkyne cannot coordinate to the metal and undergo cyclization. However, equilibration of **A** and **B** would be expected to yield some of the desired bicyclic product; thus, other factors may also be present. The more sterically crowded cobalt center might favor the more open structure **B** over a compact structure such as **A** in the equilibration of the two allyl/alkyne isomers, although facile rotation about carbon-carbon single bonds removes

**Figure 4.** Possible Insertion Geometries of Diynes into Allyl Ligands



the tether from the coordination sphere. The preference for **B** thus diverts the reaction pathway away from the production of the bicyclic product and towards a variety of unstable alternatives.

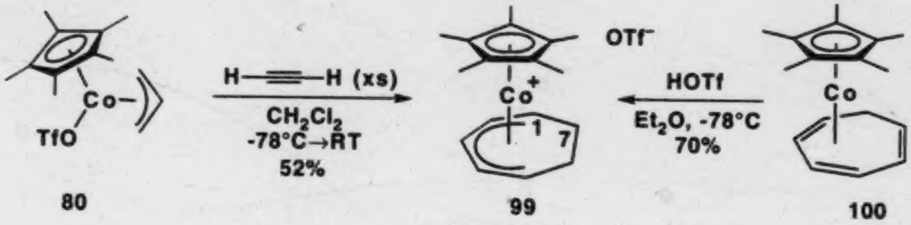
Attempts to introduce additional functional groups on the alkyne component fail to yield seven-membered ring products. Alkynes such as propargyl halides, alcohols, and ethers fail to give tractable products when allowed to react with triflate complex **80**, as do other electron rich alkynes such as alkoxyacetylenes.[107] Both Rubezhov and Etkin fail to see tractable material with the electron poor alkyne dimethylacetylenedicarboxylate.[83,89] However, with more electron rich alkynes, such as 2-butynyl acetate, a cobalticenium product is reported to form.[89] In general, this system responds well only to alkyl or aryl alkynes; the introduction of other functional groups appears to adversely affect the cobalt reactivity pattern.

### *3. [3 + 2 + 2] Acetylene/Allyl Cycloaddition Products*

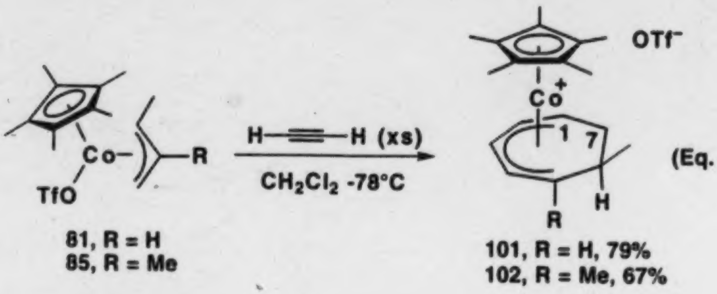
One major limitation of the iridium system[61,62] is that acetylene itself fails to react cleanly to form cycloheptadienyl complexes. Fortunately, acetylene reacts very well with the cobalt template, as initially shown by Etkin.[88,89] The rearrangement of a coordinated alkyne to a vinylidene ligand via a 1,2-hydride shift is a well known process,[108] which may occur when acetylene is allowed to react with the iridium triflate complex **37**, forming intractable product mixtures. In contrast, the less electron rich cobalt complexes do not undergo such a rearrangement, suggesting that the $\eta^2$-alkyne cobalt complex imparts greater stability to the metal than a vinylidene ligand, disfavoring the rearrangement. Another possible explanation is that the rate of the migratory insertion reaction of the cobalt allyl/alkyne intermediate is much faster than the rate of vinylidene formation.

The cobalt template **80** reacts with excess acetylene in $CH_2Cl_2$ at -78°C to give, after chromatographic workup, 52% (unoptimized) of orange cycloheptadienylcobalt complex **99**, identified by its independent synthesis from the known cycloheptatriene complex **100**[109] (Scheme **18**). Cobalt cycloheptatriene complex **100** is converted to the cycloheptadienyl complex **99** by protonation with triflic acid and characterized by $^1H$ and $^{13}C$ NMR spectroscopy. The materials are spectroscopically identical, regardless of origin.

**Scheme 18**



Since the data seem to indicate that the reaction of **80** to give [3 + 2 + 2] cycloadducts is restricted to a narrow range of alkyl or aryl substituted alkynes, the use of substituted allyl ligands becomes important for introducing greater peripheral functionality into the seven-membered ring. As discussed, synthesis of the simple 1-methyl and 1,2-dimethylallyl complexes **81** and **85** is accomplished by protonation of the diene complex resulting from ligand exchange on the bis(ethylene) complex **79** (Eq. **36**, page 34).[88,89] As also discussed, most alkynes larger than acetylene fail to give seven-membered ring products when allowed to react with crotyl compound **81**, in accord with the premise that sterically significant groups enhance the formation of five-membered ring complexes. Acetylene, however, again proved suitable for the [3 + 2 + 2] allyl/alkyne cycloaddition reaction and the synthesis of complexes **101** and **102** is readily accomplished; isolated yields of 79% and 67%, respectively, are obtained (Eq. **44**).



(Eq. 44)

The methylcycloheptadienyl complex **102** is readily identified spectroscopically as well as by comparison to the parent unsubstituted cycloheptadienyl complex **99**. The most downfield signal, at 6.73 ppm in the $^1$H NMR spectrum, is readily assigned to $H_3$. The methyl group, a doublet ($J$ = 6.7 Hz) is seen at 1.11 ppm and, by using homonuclear decoupling techniques, the multiplet centered at 0.97 ppm is found to be attached to the same carbon as the methyl group. From this starting point, the rest of the ring is readily traced using the COSY spectrum. The $H_5$ signal, a ddd multiplicity pattern at 4.31 ppm, shows a large ($J$ = 8 Hz) coupling constant to $H_4$ ($\delta$ 5.43) and two smaller ones, a 4 Hz coupling constant to $H_6$ and a W-type coupling constant of 1.2 Hz to $H_{7endo}$. The relatively small value of $J_{5\text{-}6}$ is a subtle indication that the methyl group is in an *endo* position, as the general value for $J_{5\text{-}6exo}$ is normally 4-5 Hz, while the $J_{5\text{-}6endo}$ value (Tables **1** and **2**) is substantially larger (7-8 Hz). However, NOE experiments fail to provide conclusive evidence for the stereochemistry of the methyl group and ultimately, this assignment is based on the crystal structure of the bicyclic system **111**, which unambiguously shows the ring juncture in an *endo* geometry. The gated decoupled $^{13}$C NMR spectrum of this compound (**101**) is relatively straightforward, showing the five downfield doublets expected of an unsubstituted pentadienyl at $\delta$ 100.8 ($C_3$), 98.6 ($C_2$), 98.3 ($C_4$), 96.9 ($C_5$), and 89.7 ($C_1$). Of these, two signals have smaller values for $^1J_{CH}$: the $\delta$ 96.9 ($J$ = 154 Hz) and $\delta$ 89.7 ($J$ = 154 Hz) resonances. These two carbons are thus assigned to the terminal positions of the pentadienyl fragment. Heteronuclear correlated spectroscopy is used to make the final assignments of these carbon atoms. The two sp$^3$

carbons of the cycloheptadienyl ligand, although not particularly unusual in chemical shift ($\delta$ 36.6 and $\delta$ 47.6) have somewhat unexpected assignments. The anisotropic effects of the Cp* ring and the metal must affect the environment of these carbons more than the amount of substitution, as it would be expected that a trisubstituted carbon would resonate further downfield than a disubstituted carbon. However, the signal at $\delta$ 36.6 is a doublet ($J$ = 125 Hz) in the gated decoupled spectrum and the HETCORR spectrum indicates that this carbon is attached to the $H_6$ proton: two pieces of data that assign this signal to $C_6$. Surprisingly, this trisubstituted carbon has a higher field chemical shift than the disubstituted $C_7$, which is found at $\delta$ 47.6 (t, $^1J_{CH}$ = 128 Hz). The $C_7$ assignment is also further confirmed by the HETCORR spectrum, linking it directly to both $H_7$ protons at $\delta$ 2.44 ($H_{7endo}$) and $\delta$ 1.95 ($H_{7exo}$).

The *endo* geometry of this complex is further confirmed by the synthesis of the corresponding *exo*-methyl complex, obtained in two steps from the parent unsubstituted cycloheptadienyl complex. Complex **99** was first treated with MeLi in THF. This product was not characterized, but immediately treated with trityl tetrafluoroborate in $CH_2Cl_2$ to give *exo*-**101** in moderate (29%) unoptimized yield. By $^1$H NMR spectroscopy, the two complexes are clearly different. For example, the chemical shifts of the three hydrogen atoms on the methylene carbons of the cycloheptadienyl ring in the *exo*-complex are 3.13, 1.80 and -0.19 ppm. In contrast, the corresponding values for the *endo*-complex are 2.44, 1.95 and 0.97 ppm.

Dimethylcycloheptadienyl complex **102** shows similar spectroscopic patterns to **101**; however, only four downfield resonances are observed in the $^1$H NMR spectrum, at $\delta$ 6.67 ($H_3$), 5.34 ($H_4$), 5.00 ($H_2$), and 4.46 ($H_1$). The $H_4$ signal is a cleanly resolved doublet ($J_{4\text{-}3}$ = 6.5 Hz), suggesting that it is adjacent to the methyl group on $C_5$. Again, the COSY spectrum assists the assignment of the signals along the ring starting from $H_4$. Direct connectivity is established along the ring system by a series of correlations, *i.e.* 5.34 ($H_4$) $\leftrightarrow$ 6.67 ($H_3$) $\leftrightarrow$ 5.00 ($H_2$) $\leftrightarrow$ 4.46 ($H_1$) $\leftrightarrow$ 2.41 ($H_{7endo}$) and 1.8 ($H_{7exo}$). The sole remaining non-methyl signal is assigned to $H_6$. Tentative assignment of the methyl group stereochemistry is provided only by the chemical shift of the $H_6$ proton ($\delta$ 0.90), which is significantly shifted upfield, suggesting an *exo* position. More substantial evidence for this stereochemistry is obtained by the comparison of the similar $^1H$ NMR spectroscopic features to those of **111** (Table **2**), for which an X-ray crystal structure provides proof of the *endo* stereochemistry. Due to the multiplet character of both $H_6$ and $H_{7exo}$, $J_{6\text{-}7exo}$ could not be obtained, which would have helped to confirm the relative position of $H_6$. The two methyl groups on the cycloheptadienyl ligand are found at $\delta$ 1.55 (s, 3H), a chemical shift suggesting attachment to an $sp^2$ hybridized carbon atom, and $\delta$ 1.05 (d, $J = 7$ Hz), assigning the latter group to the $C_6$ position by the doublet multiplicity.

Attempts to verify the stereochemistry at carbon 6 in cycloheptadienyl complex **102** by NOE spectroscopy gives, at best, inconclusive data. Irradiation of the Cp* singlet of **102** at $\delta$ 1.96 shows NOE enhancement for the hydrogen atoms of the pentadienyl fragment of 5-10%. Unfortunately, no other signal shows definite NOE enhancement. Due to the extensive number of large coupling constants for these signals, each is relatively wide (25-35 Hz). Perhaps a small enhancement (over a wide area) of the signal is simply not resolved. It is equally probable that the methylene protons are in fact too far from the $C_5Me_5$ ligand to show noticeable NOE effects. A similar lack of conclusive results is obtained from NOE experiments using the bicyclic complex **111**.

Corroborating evidence for the proposed structure of this product is provided from additional deuteration studies (Scheme **19**). Reaction of the isoprene complex **83** with deuterated triflic acid gives the monodeuterated dimethylallyl complex **85-d$_1$**, which was used without further characterization. Subsequent reaction with acetylene provides cycloheptadienyl complex **102-d$_1$**. The product and position of deuteration were identified using both $^1H$ and $^2H$ NMR spectra. Deuterium is located only on the *endo*

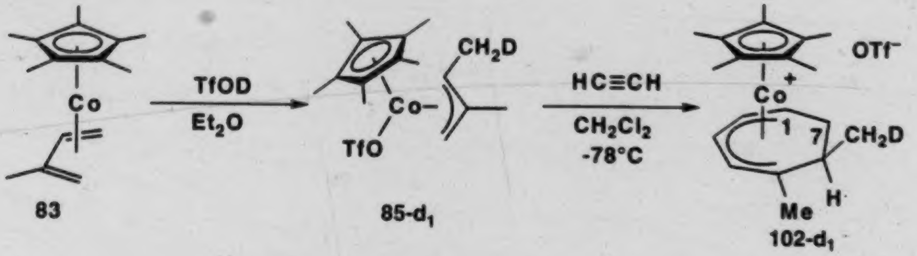
**Table 2.** Comparative $^1$H NMR Spectroscopic Data For Acetylene Derived Cp* $\eta^5$-Cycloheptadienyl Complexes

| | 99 | 101 | 102 | 105 | 111 | 117 |
|---|---|---|---|---|---|---|
| $H_1$<br>$J_{1\text{-}2}$ | 4.42 (m)<br>8.6 Hz | 4.56 (ddd)<br>9.2 Hz | 4.46 (ddd)<br>8.7 Hz | 4.18 (dt)<br>9.6 Hz | 4.47 (dtd)[c]<br>9.2 Hz | 4.41 (m)<br>9.1 Hz |
| $H_2$<br>$J_{2\text{-}3}$ | 5.02 ("t")<br>6.7 Hz | 5.13 ("t")<br>6.8 Hz | 5.00 (t)<br>6.7 Hz | 4.66 (t)<br>8.4 Hz | 4.86 (ddd)<br>7.1 Hz | 4.88 (dd)<br>7.3 Hz |
| $H_3$<br>$J_{3\text{-}4}$ | 6.51 ("t")<br>6.7 Hz | 6.73 ("t")<br>6.2 Hz | 6.67 ("t")<br>6.2 Hz | 6.55 (t)<br>6.0 Hz | 6.69 (dd)<br>6.1 Hz | 7.04 (dd)<br>6.6 Hz |
| $H_4$<br>$J_{4\text{-}5}$ | 5.02 ("t")<br>8.6 Hz | 5.43 ("t")<br>7.9 Hz | 5.34 (d)<br>b | 5.39 (d)<br>b | 5.44 (d)<br>b | 6.51 (d)<br>b |
| $H_5$<br>$J_{5\text{-}6endo}$<br>$J_{5\text{-}6exo}$ | 4.42 (m)<br>a<br>a | 4.31 (ddd)<br>b<br>3.8 Hz | b | b | b | b |
| $H_{6endo}$<br>$J_{6endo\text{-}6exo}$<br>$J_{6endo\text{-}7endo}$<br>$J_{6endo\text{-}7exo}$ | 2.42 (m)<br>10 Hz<br>a<br>a | b | b | b | b | b |
| $H_{6exo}$<br>$J_{6exo\text{-}7endo}$<br>$J_{6exo\text{-}7exo}$ | 1.20 (m)<br>a<br>a | 0.97 (m)<br>8.6 Hz<br>a | 0.90 (m)<br>8.8 Hz<br>a | 0.55 (m)<br>10.2 Hz<br>4.2 Hz | 0.38 (dddd)[c]<br>10.8 Hz<br>4.8 Hz | 0.77 (m)<br>11.3 Hz<br>4 Hz |
| $H_{7endo}$<br>$J_{7endo\text{-}7exo}$<br>$J_{7endo\text{-}1}$ | 2.42 (m)<br>a<br>a | 2.44 (ddd)<br>16 Hz<br>1.2 Hz | 2.41 (ddd)<br>16 Hz<br>4.4 Hz | 2.46 (ddd)<br>17.4 Hz<br>3.6 Hz | 2.66 (ddd)<br>17.1 Hz<br>3.6 Hz | 2.90 (ddd)<br>17 Hz<br>3.3 Hz |
| $H_{7exo}$<br>$J_{7exo\text{-}1}$ | 1.20 (m)<br>a | 1.95 (m)<br>a | 1.8 (m)<br>a | 2.34 (ddd)<br>4.2 Hz | 2.26 (dddd)[c]<br>3.6 Hz | 2.12 (d)<br>4 Hz |

[a] Numerical value for the coupling constant was not obtained due to second order character or complexity of the signal. [b] Not applicable due to a non- hydrogen substituent. [c] Additional splitting observed due to long range coupling.

methyl group, suggesting that the formation of the cycloheptadienyl ligand is a selective process; the two methyl groups remain inequivalent.

**Scheme 19**


Co
83
TfOD
Et₂O
CH₂D
Co
TfO
85-d₁
HC≡CH
CH₂Cl₂
-78°C
OTf⁻
Co⁺
1
7
CH₂D
H
Me
102-d₁

Other apparently simple allyl complexes fail to react cleanly with acetylene. Cinnamyl complex **91** and the carbomethoxyallyl **92** both fail to yield tractable material when allowed to react with acetylene under otherwise identical reaction conditions used for the synthesis of **101** and **102**. One possible explanation is that the coordination of the phenyl ring or ester carbonyl to the unsaturated cobalt center competes with the coordination of the alkyne, thus preventing the formation of cycloheptadienyl products (Figure 5). However, the similar failure of the 1,3-dimethylallyl complex **86** and, surprisingly, 2-methylallyl complex **90** to yield cycloheptadienyl products upon treatment with acetylene suggests that other factors besides chelation are in effect.

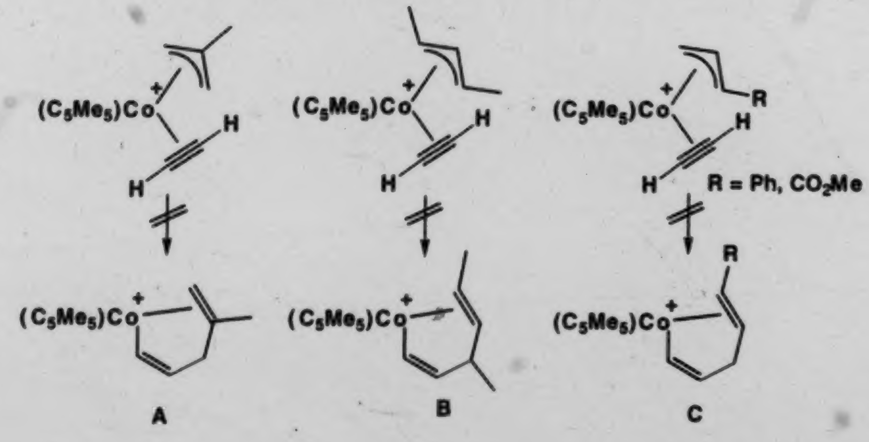
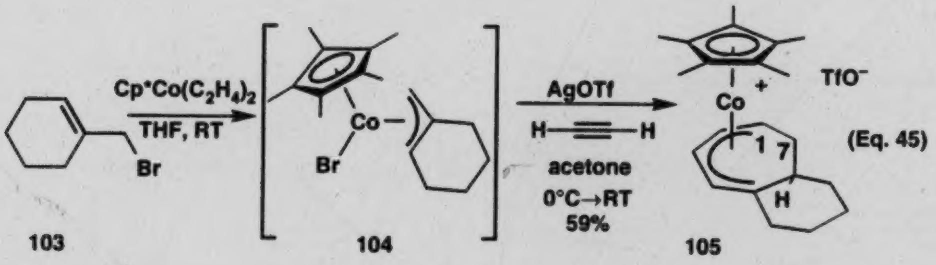

(C₅Me₅)Co⁺
H
H
(C₅Me₅)Co⁺
H
H
(C₅Me₅)Co⁺
R
H
H
R = Ph, CO₂Me
(C₅Me₅)Co⁺
(C₅Me₅)Co⁺
(C₅Me₅)Co⁺
R
A
B
C

**Figure 5.** Coordination of Pendant Olefin Groups

The failure of substituted allyl complexes **86** and **90** to react with acetylene to yield $\eta^5$-cycloheptadienyl products may be due to the difficulty in coordinating the tethered alkene in the pre-cyclized intermediate (**A** and **B** in Figure **5**). Substituted alkenes generally are weaker donors to metal complexes than non-substituted alkenes, due to steric repulsion of the larger alkene with ancillary ligands ($C_5Me_5$) on the metal. Electron withdrawing groups (phenyl, carbomethoxy) may inhibit the tethered alkene from coordinating (**C** in Figure **5**), thus preventing cyclization. This process presumably leads to a variety of decomposition products, given the assumption that the simple vinyl complex is unstable. However, it may be assumed that initial coordination and insertion proceed, based on the complete disappearance of the starting allyl complexes.

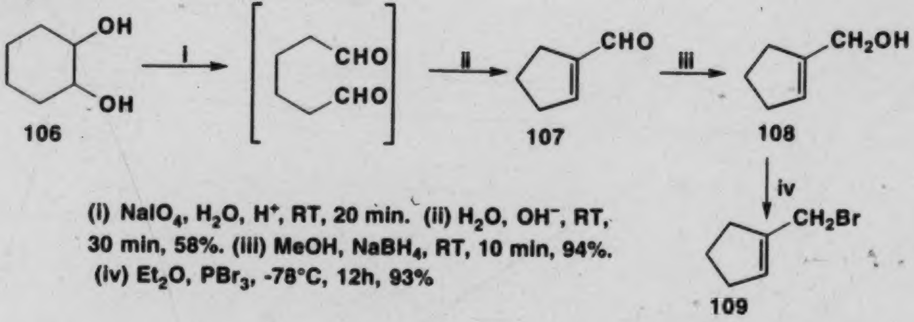
However, given this explanation, the 1,2-dimethylallyl complex **85** would also not be expected to produce cycloheptadienyl complex **102**, so it appears that very subtle effects govern the course of the reaction. Further research into the effects of substituents on the allyl ligand is currently planned.

Encouraged by the success of the 1,2-dimethylallyl system, more complex molecules were targeted. Due to the large number of polycyclic natural products[25] containing a seven-membered ring fused to a five- or six-membered ring, it was decided to try cyclic allyl ligands in the [3 + 2 + 2] allyl/alkyne cycloaddition process, reasoning that the product from such a process would be a model for other fused ring systems. The preparation of 1-(bromomethyl)-1-cyclohexene (**103**) is accomplished by NBS bromination[110] of methylenecyclohexane[111] in $CCl_4$ solvent. Other methods have also been used to synthesize **103**.[74g] Under the reaction conditions, the reaction of the allylic radical intermediate apparently favors the formation of the more highly substituted olefin. Oxidative addition of **103** to $(\eta^5\text{-}C_5Me_5)Co(C_2H_4)_2$ **79** is carried out in tetrahydrofuran solution, forming a dark red-purple complex **104** (Eq. **45**). The exocyclic allyl complex **104** is thermally sensitive, decomposing to unidentified paramagnetic materials over the course of a few days. Consequently, the procedure was modified to avoid isolation of this unstable allyl complex. *In situ* ionization of crude **104** by silver tetrafluoroborate or silver triflate followed by the addition of excess acetylene gives moderate overall yields of bicyclo[5.4.0]decadienyl complex **105** (Eq. **45**). Characterization of the bicyclic system is complicated by the presence of several overlapping multiplets in the $^1$H NMR spectrum. However, 2-dimensional NMR spectroscopy unambiguously defines the structure as compound **105**. Studies of NOE enhancement, however, as with cycloheptadienyl complex **101**, fail to distinguish between the *endo* and *exo* stereochemistry at the five-seven ring juncture in **105**. Once again, only the protons on the pentadienyl framework show strong enhancements of between 5-10%.



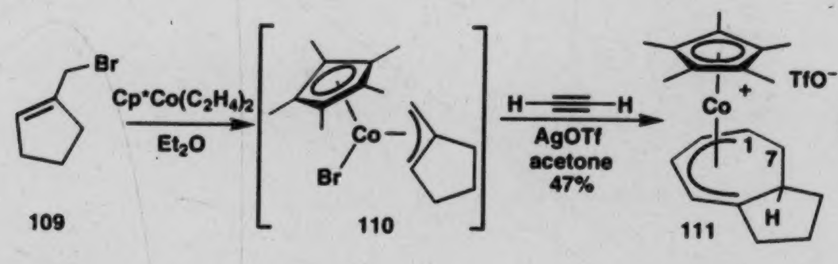
To extend the synthesis of these interesting bicyclic cycloheptadienyl complexes, 1-(bromomethyl)cyclopentene **109** was synthesized in several steps from cyclohexanediol, using a known procedure (Scheme **20**).[112,113] Following the method of Brown, cyclopentenecarboxaldehyde (**107**) is prepared from cyclohexanediol (**106**) by an oxidative ring fission using $NaIO_4$, after which the intermediate adipaldehyde undergoes base-catalyzed aldol cyclization.[112] The reduction of cyclopentenecarboxaldehyde with $NaBH_4$ in methanol gives the allylic alcohol **108**.[113] Bromination of alcohol **108** is accomplished by the reaction with $PBr_3$ in diethyl ether at -78°C to provide bromide **109**.[113] 1-(Bromomethyl)-1-cycloalkenes have also been prepared by other routes.[74g]

Scheme 20



(i) $NaIO_4$, $H_2O$, $H^+$, RT, 20 min. (ii) $H_2O$, $OH^-$, RT, 30 min, 58%. (iii) MeOH, $NaBH_4$, RT, 10 min, 94%. (iv) $Et_2O$, $PBr_3$, -78°C, 12h, 93%

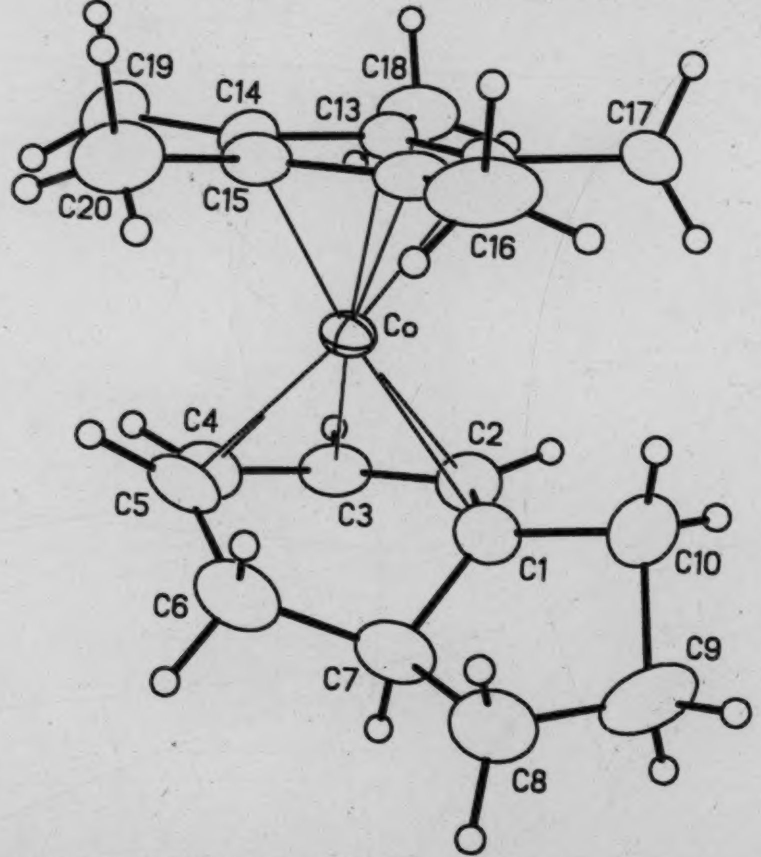
Allowing ($\eta^5$-$C_5Me_5$)Co($C_2H_4$)$_2$ (**79**) to react with **109** yields an uncharacterized purple complex **110** presumed to be similar to exocyclic allyl complex **104** (Eq. **46**). This reaction is followed immediately by *in situ* ionization of the intermediate allyl halide complex with silver salts in the presence of excess acetylene to give the pentahydroazulenyl system **111**. The full array of NMR spectroscopic techniques was



(Eq. 46)

used to establish the structure, aside from defining the stereochemistry of the ring juncture. To make this last assignment, X-ray quality crystals were grown from dichloromethane/diethyl ether. A crystal structure determination was carried out, unambiguously defining the $C_6$ ring juncture as *endo*, giving the first clear confirmation of the stereochemistry of the ring junction. Salient features of the crystal structure are given in Figure **6**.[115] This structure provides the basis for the stereochemical assignment of other cycloheptadienyl complexes, notably the methyl- and dimethylcycloheptadienyl complexes **101** and **102**. Using the Karplus relationship, the bond angles from the crystal structure can provide an estimate of coupling constants observed in the $^1$H NMR

**Figure 6**. ORTEP[115] for Complex **111** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS9711



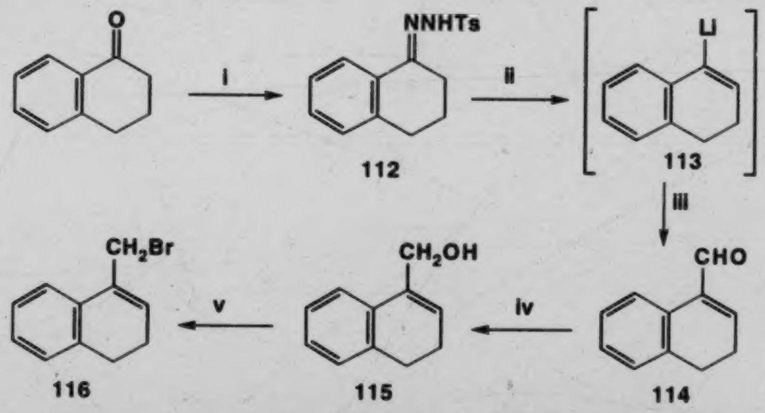
Final Residuals: $R_1 = 0.1103$; $wR_2 = 0.2744$. Data obtained at -60°C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.
Selected Bond Distances (Å): Co-C1, 2.255(11); Co-C2, 2.032(9); Co-C3, 2.031(8); Co-C4, 2.031(9); Co-C5, 2.067(10); C1-C2, 1.451(14); C1-C7, 1.466(15); C1-C10, 1.50(2); C2-C3, 1.421(15); C3-C4, 1.386(15); C4-C5, 1.380(15); C5-C6, 1.49(2); C6-C7, 1.54(2); C7-C8, 1.56(2); C8-C9, 1.47(2); C9-C10, 1.57(2).

Selected Bond Angles (deg.): C2-C1-C7, 125.2(10); C2-C1-C10, 119.0(11); C7-C1-C10, 109.9(10); C1-C2-C3, 120.9(10); C2-C3-C4, 123.3(9); C3-C4-C5, 126.4(11); C4-C5-C6, 133.9(12); C5-C6-C7, 108.7(10); C1-C7-C6, 113.6(10); C1-C7-C8, 106.5(10); C6-C7-C8, 110.2(11); C7-C8-C9, 98.6(10); C8-C9-C10, 105.7(11); C1-C10-C9, 98.7(11).

spectrum, provided the solid state and solution structure remain similar. It can be seen in Table **2** that the assignment of an *endo* alkyl group fits the spectroscopic data for both **101** and **102**.

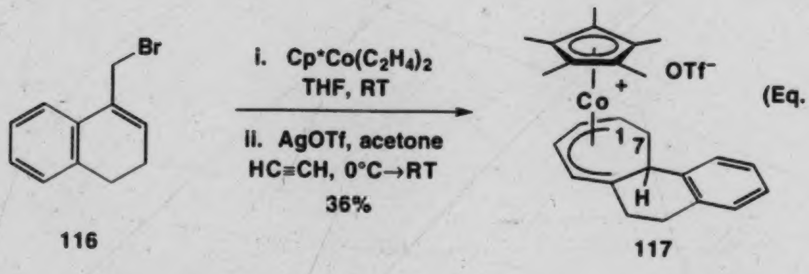
A third cyclic template was synthesized from the tetralone-derived allylic halide **116** (Scheme **21**). Allowing tetralone to react with tosylhydrazine hydrochloride forms the tosylhydrazone **112**, which is treated with BuLi under Shapiro reaction conditions,[102] forming the intermediate vinyllithium complex **113**. Quenching this intermediate with DMF provides the vinylcarboxaldehyde **114**. Reduction using $NaBH_4$ in methanol yields the allylic alcohol **115**, which is brominated with $PBr_3$ to produce the bromide **116**. The analogous allyl fluoride compound has been prepared using different methodology.[114a] Allyl alcohol **115** has previously been prepared using a similar procedure.[114b,c]

**Scheme 21**



i) $NH_2NHTs$, $H^+$, ethanol, 96%. ii) BuLi (3eq.), THF -78°C. iii) DMF, -78°C, 39%. iv) $NaBH_4$, methanol, quant. v) $PBr_3$, -78°C, ether, 36%

The reaction of bromide **116** with the bis(ethylene) complex **79** provides a dark purple-black intermediate cobalt allyl halide complex, which was not characterized, but allowed to react further with silver triflate in the presence of excess acetylene (Eq. **47**). The cycloheptadienyl product **117** is isolated in rather low yield, although the remainder of the material balance is of unknown composition. It is possible that the cobalt allyl complex formed is even less stable than previous exocyclic allyls and that substantial decomposition occurs before ionization and cyclization can take place.

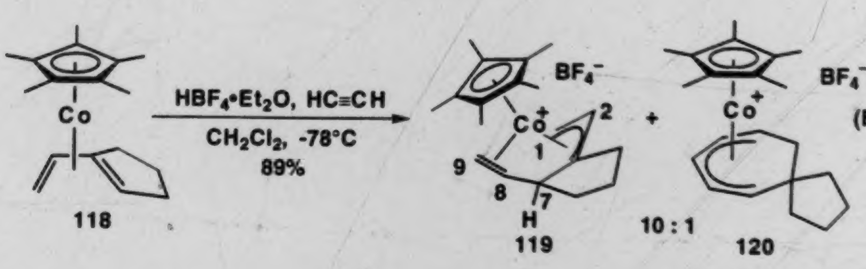


116 117

(Eq. 47)

Having shown that bicyclic compounds can easily be made, an attempt was made to form a spirocyclic compound using 1-vinyl-1-cyclopentene (Eq. **48**).[116] Thermal displacement of the ethylene ligands of **79** by 1-vinyl-1-cyclopentene is easily accomplished to yield **118** as a highly air sensitive red solid. Protonation of this diene complex with $HBF_4{\bullet}Et_2O$ ($CH_2Cl_2$, -78°C) is followed by addition of excess acetylene, giving complex **119** as the major product after isolation and purification by recrystallization from dichloromethane/diethyl ether. The $^1H$ NMR spectrum indicates the presence of two distinct AMX spin coupling patterns. The furthest downfield signal at $\delta$ 4.18 ($H_2$) is spin coupled to two other signals at $\delta$ 3.44 ($H_{1syn}$) and $\delta$ 0.98 ($H_{1anti}$) with coupling constants of 8.0 Hz and 12.3 Hz, respectively. The two upfield signals in this pattern are also mutually coupled ($J_{1a\text{-}1s}$ = 2.5 Hz). The $H_1$ hydrogen atoms are shown by the HMQC spectrum to be located on the same carbon, which is evidently $sp^2$ hybridized ($^1J_{CH}$ = 162 Hz). The $H_2$ signal is also located on an $sp^2$ hybridized carbon at $\delta$ 86.0 ($^1J_{CH}$ = 163 Hz). The HMBC spectrum indicates that a quaternary carbon is adjacent to these signals by correlations from all three proton signals to $\delta$ 81.1 ($C_3$), a singlet in the $^{13}C$ spectrum.

The other diagnostic AMX pattern consists of a signal at $\delta$ 2.75 ($H_8$) which shows coupling to both a signal at $\delta$ 3.18 ($H_{9syn}$) ($J$ = 7.9 Hz) and to an obscured signal at $\delta$ 1.95 ($H_{9anti}$) ($J$ = 13.7 Hz). Heteronuclear correlated spectra show that these hydrogen atoms are attached to carbon atoms that resonate at 62.9 ppm ($C_9$) and 42.3 ppm ($C_8$), which are both $sp^2$ hybridized, as shown by the $^1J_{CH}$ values of 160 and 166 Hz, respectively. The two fragments are connected by a single carbon link, $C_7$ (37.0 ppm, d, $J = 144$ Hz), which has an attached proton at $\delta$ 0.91, with a coupling constant to $H_8$ of 7.6 Hz, a $^2J_{CH}$ to the quaternary $C_3$, and a $^3J_{CH}$ to $C_2$, the latter two couplings obtained from the HMBC spectrum.

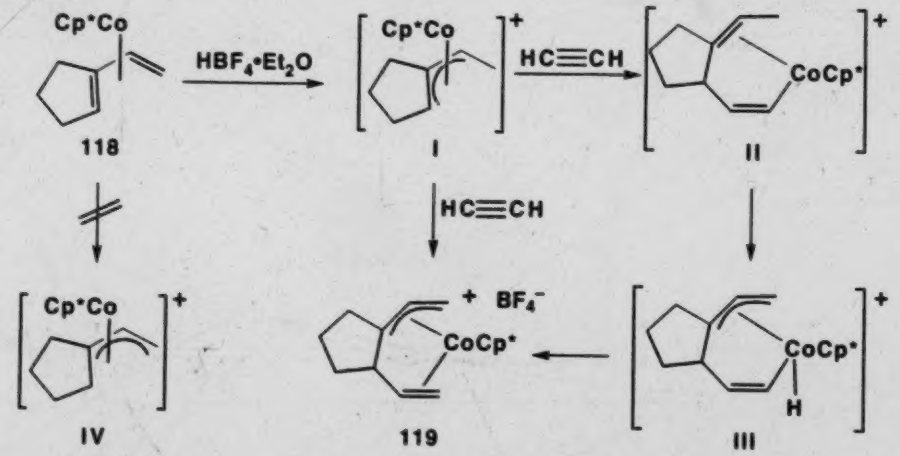


(Eq. 48)

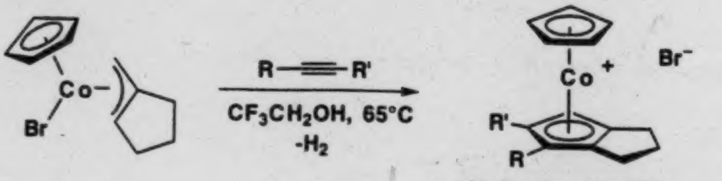
A minor product is also observed in the $^1$H NMR spectrum of complex **120**, which is tentatively assigned as the desired spirocyclic seven-membered ring product based on its $^1$H NMR spectrum. However, as the two complexes are formed in approximately a 10:1 ratio favoring the allyl olefin complex **119** and several signals are obscured, very little else can be said about complex **120**.

It is somewhat surprising that in the major product, only one equivalent of acetylene is taken up by the metal, in contrast to the large number of [3 + 2 + 2] cycloaddition reactions with cobalt allyl complexes and acetylene that we have observed. Protonation probably initially occurs on the metal, followed by hydride migration to the vinyl portion of the ring, forming preferentially an *anti*-methylallyl complex (**I**, Scheme **22**), rather than the desired allyl complex (**IV**) which would lead to a spirocyclic compound upon reaction with two equivalents of acetylene. This pattern is consistent with the protonation of the cobalt isoprene complex **83** to give 1,2-dimethylallyl complex **85**; in both cases a 1,1-disubstituted allyl is disfavored. Insertion of one equivalent of acetylene into **I** gives a vinyl olefin complex **II**, in which C-H activation is evidently the favored process; intermediate **III** forms faster than coordination and insertion of a second equivalent of acetylene. In this particular cobalt template, it is likely that the *anti* methyl group is positioned very close to the metal, facilitating C-H activation. Reductive elimination of the vinyl and hydride ligands in complex **III** forms the isolated $\eta^3,\eta^2$-complex **119**. Several attempts were made to duplicate this reactivity pattern with 2-butyne but no tractable products could be obtained. Furthermore, heating the allyl complex **119** at ($CH_2Cl_2$, 40°C, sealed vessel) in an acetylene atmosphere did not induce any further reaction.

**Scheme 22**



It was thought that exocyclic allyl complexes would show a decreased tendency to form five-membered rings from a single insertion of alkyne, due to the steric strain built up in a bicyclo [3.3.0] system (Eq. **49**). However, when a five-membered exocyclic allyl complex analogous to **110** reacts with 2-butyne in trifluoroethanol, a mixture of products is formed, one of which is characterized as the yellow bicyclo[3.3.0]octadienyl complex **121** by its $^1H$ and $^{13}C$ NMR spectra after purification by chromatography and recrystallization. Formation of a seven-membered ring product is not observed. Similar results are obtained in the reaction with *t*-butylacetylene, which yields the five-membered ring product **122** (Eq. **49**) in moderate yield.



121 R = R' = Me, 22%
122 R = H, R' = *t*-Bu, 51%

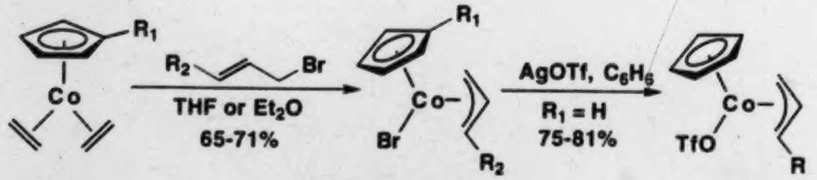
(Eq. 49)

Although the reaction of cobalt allyl complex **80** with alkynes does not show great tolerance for functional groups on the alkyne, acetylene readily reacts to form [3 + 2 + 2] cycloadducts. In addition, a fairly wide range of allyl ligands undergo clean reaction with acetylene to give various substituted mono- and bicyclic seven membered ring products.

### *4. [3 + 2 + 2] Cycloaddition Reactions Using Non-$C_5Me_5$ Cobalt Allyl Templates*

The limitations based on the steric profile of the alkyne that are encountered in the Cp* system prompted an investigation into the chemistry of the analogous $\eta^5$-cyclopentadienylcobalt system. Due to the much smaller size of the cyclopentadienyl ligand, it was hoped that more general reactivity would be seen, as a lower steric barrier to coordination should exist. The use of the more readily available cyclopentadienyl ligand is also an advantage for large scale synthesis. The main concern was whether the decreased steric profile would lead to mixtures of $\eta^5$-cycloheptadienyl and $\eta^1,\eta^4$-methanocyclohexadiene complexes.

Cyclopentadienyl cobalt allyl complex **125** is readily prepared from $CpCo(C_2H_4)_2$ (**123**) and allyl bromide in a known oxidative addition reaction.[117] The procedure is readily adapted to produce other allyl complexes **126** and **127** as well as methylcyclopentadienyl complexes **128** and **129** (Eq. **50**).[117] The cyclopentadienylcobalt allyl triflate **130** is prepared in 81% yield by silver triflate metathesis from $(C_5H_5)Co(\eta^3$-allyl)Br (**125**).[93e,f] Unlike the corresponding iridium reactions,[83d,91] in which two equivalents of silver were required for clean conversion to the triflate complex, the reaction of **125** with silver triflate takes place smoothly in benzene solvent using only a slight excess of silver triflate. The allyl stereochemistry is assumed to be *exo* "point up" based on comparison to known iridium allyl complexes, and the allyl substituent is assigned as *syn* by the $^1$H NMR coupling constants.[62] The crude product could be recrystallized from toluene/pentane at low temperature and, although homogeneous by $^1$H NMR spectroscopy, the combustion analysis of the recrystallized material indicates the presence of a slight impurity. Given the comparable solubilities of silver triflate and **130**, silver contamination of the product is assumed. In spite of this impurity, further reactivity is not adversely affected. This method proves to be general for the synthesis of several different allyl complexes with variations in both cyclopentadienyl and allyl ligands (Eq. **50**).



(Eq. 50)

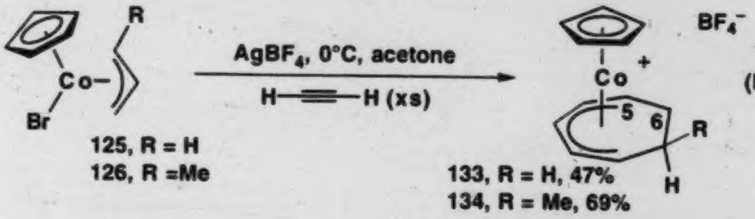
**123** $R_1 = H$
**124** $R_1 = Me$

**125** $R_1, R_2 = H$
**126** $R_1, R_2 = H, Me$
**127** $R_1, R_2 = H, Ph$
**128** $R_1, R_2 = Me, H$
**129** $R_1, R_2 = Me$

**130** $R = H$
**131** $R = Me$
**132** $R = Ph$

Although complex **130** yields the light orange cycloheptadienyl complex **133** when allowed to react with acetylene in dichloromethane, this [3 + 2 + 2] cycloaddition reaction is more readily carried out using *in situ* ionization of the allyl cobalt bromide complex **125** with silver tetrafluoroborate (Eq. **51**). The cycloheptadienyl product **133** is identified by comparison of the $^1$H NMR spectrum with the pentamethylcyclopentadienyl analogue, as well as the full array of spectroscopic and analytical techniques, but requires more extensive purification relative to the pentamethylcyclopentadienyl analogue. Complex **133** can also be formed from protonation of the cycloheptatriene complex. ($\eta^5$-Cyclopentadienyl)($\eta^5$-cycloheptadienyl)cobalt(III) cations and ($\eta^5$-

cyclopentadienyl)cobalt($\eta^4$-cycloheptatriene) have both been made using a different route, starting with intact seven-membered ring organic substrates.[118] Reaction of the crotyl complex **126** with $AgBF_4$ and acetylene gives a high yield of complex **134** after chromatography, but this material required additional purification by additional chromatography and recrystallization for the combustion analysis sample.



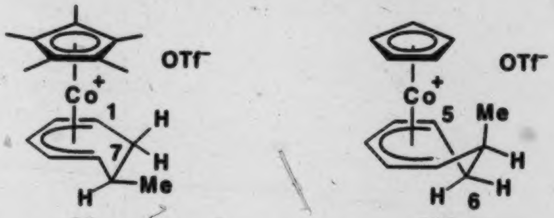
125, R = H
126, R =Me

133, R = H, 47%
134, R = Me, 69%

(Eq. 51)

The $^1H$ NMR spectra for these (cyclopentadienyl)cobalt cycloheptadienyl complexes differ slightly from those of the Cp* analogues. The conformation of the $C_5Me_5$ cycloheptadienyl system assigns the $H_{6exo}$ proton as having the furthest upfield chemical shift and accordingly, the substituents in the $C_5Me_5$ system are assigned to the $C_5$ and $C_6$ positions. Although the substitution pattern of the cycloheptadienyl complexes in the $C_5H_5$ system is identical to the $C_5Me_5$ cycloheptadienyl patterns, the conformation is apparently different (Figure 7). Thus, to facilitate spectroscopic comparison between the two systems, the numbering scheme for the $C_5H_5$ complexes is based on the conformation and ignores the substitution pattern. This maintains the assumed conformational geometry and the relative values of both the chemical shifts and

**Figure 7.** Conformational Differences in Cp and Cp* Cycloheptadienyl Complexes.



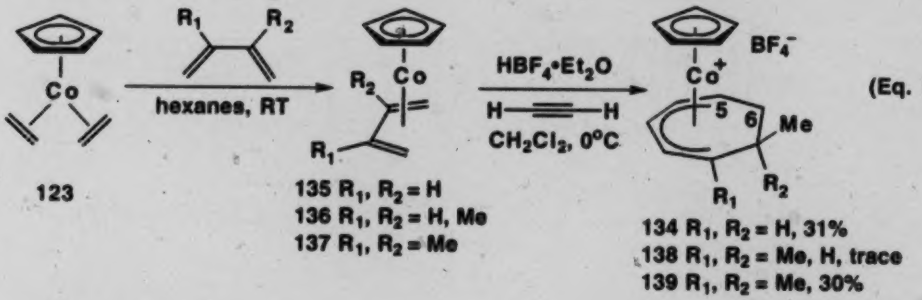
99

134

coupling constants. Although the difference in the numbering scheme now maintains the atoms in similar chemical environments to those assumed in the Cp* system, the substituents thus become assigned to apparently different positions.

The bicyclic complex **143** appears to be the sole exception to this conformational change, as the $^1$H NMR data best fit the conformational pattern exhibited by the pentamethylcyclopentadienyl complexes, and is thus assigned a 5,6-substitution pattern (Table **3**). The other cyclopentadienyl complexes all appear to maintain a conformation that conforms to a 1,7-substitution pattern based on the available spectral data for the cycloheptadienyl products.

Cyclopentadienyl cobalt allyl complexes are not readily made by the protonation of coordinated dienes, in contrast to their $C_5Me_5$ counterparts. Some difficulty with low yields and intractable product mixtures is encountered upon protonation of CpCo(diene) complexes.[119] However, a more successful approach to [3 + 2 + 2] cycloaddition reactions is the *in situ* protonation of cobalt diene complexes in the presence of acetylene (Eq. **52**). Cobalt butadiene, isoprene and 2,3-dimethylbutadiene complexes **135**-**137** are all easily formed from the thermal (room temperature) exchange with the ethylene ligands of $CpCo(C_2H_4)_2$ (**124**) and may be isolated at this stage as discrete cobalt(I) diene complexes (Eq. **52**). The protonation of complexes **135** and **137** by $HBF_4 \cdot Et_2O$ is followed by the addition of acetylene, resulting in the formation of cycloheptadienyl complexes **134** and **139**, albeit in moderately low yield. Vicinal



123

135 R1, R2 = H
136 R1, R2 = H, Me
137 R1, R2 = Me

134 R1, R2 = H, 31%
138 R1, R2 = Me, H, trace
139 R1, R2 = Me, 30%

(Eq. 52)

**Table 3.** Comparative $^1H$ NMR Spectroscopic Data for Acetylene Derived Cycloheptadienyl Complexes with Cyclopentadienyl Ligands

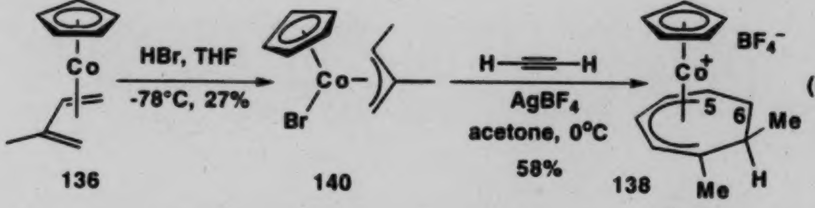
| | **133** | **134** | **138** | **139** | **143** | **144** |
|---|---|---|---|---|---|---|
| **$H_1$**<br>$J_{1\text{-}2}$ | 5.60 (m)<br>6 Hz | 5.31 (dd)<br>8.7 Hz | b | b | 5.35 (m)<br>a | b |
| **$H_2$**<br>$J_{2\text{-}3}$ | 5.80 (t)<br>6.6 Hz | 5.75 (t)<br>6.6 Hz | 5.55 (d)<br>6.6 Hz | 5.26 (d)<br>6.8 Hz | 5.35 (m)<br>6.3 Hz | 5.33 (d)<br>7.9 Hz |
| **$H_3$**<br>$J_{3\text{-}4}$ | 7.41 (t)<br>6.6 Hz | 7.41 (t)<br>6.6 Hz | 7.18 (dd)<br>6.9 Hz | 7.29 (dd)<br>5.3 Hz | 7.24 (t)<br>6.3 Hz | 7.19 (ddd)<br>6.1 Hz |
| **$H_4$**<br>$J_{4\text{-}5}$ | 5.80 (t)<br>6.6 Hz | 5.80 (t)<br>7 Hz | 5.67 (dd)<br>7.4 Hz | 6.15 (dd)<br>6.6 Hz | 6.04 (d)<br>b | 5.86 (dd)<br>7.8 Hz |
| **$H_5$**<br>$J_{5\text{-}6endo}$<br>$J_{5\text{-}6exo}$ | 5.60 (m)<br>a<br>a | 5.49<br>6.3 Hz<br>4.0 Hz | 5.28 (m)<br>6.0 Hz<br>4.6 Hz | 5.13 (m)<br>8.4 Hz<br>6.6 Hz | b | 5.24 (m)<br>7.6 Hz<br>4.5 Hz |
| **$H_{6endo}$**<br>$J_{6endo\text{-}6exo}$<br>$J_{6endo\text{-}7endo}$<br>$J_{6endo\text{-}7exo}$ | 2.49 (m)<br>a<br>a<br>a | 2.09 (dtd)<br>14.9 Hz<br>b<br>5.5 Hz | 2.06 (ddd)<br>14.9 Hz<br>b<br>5.9 Hz | 1.46 (dd)<br>12.6 Hz<br>b<br>b | b | 1.8$^c$ (m)<br>13.4 Hz<br>b<br>a |
| **$H_{6exo}$**<br>$J_{6exo\text{-}7endo}$<br>$J_{6exo\text{-}7exo}$ | 1.25 (m)<br>a<br>a | 1.30 (dtd)<br>b<br>4.2 Hz | 1.15 (dddd)<br>b<br>4.8 Hz | 0.11 (dd)<br>b<br>b | 0.80 (m)<br>9.9 Hz<br>6.1 Hz | 0.75 (m)<br>b<br>6.7 Hz |
| **$H_{7endo}$**<br>$J_{7endo\text{-}7exo}$<br>$J_{7endo\text{-}1}$ | 2.49 (m)<br>a<br>a | b | b | b | 2.84 (ddd)<br>17.6<br>3.8 | b |
| **$H_{7exo}$**<br>$J_{7exo\text{-}1}$ | 1.25 (m)<br>a | 1.57 (m)<br>3.5 Hz | 1.45 (m)<br>b | b | 2.32 (ddd)<br>2.2 | 1.8$^c$ (m) |

[a] Numerical value for the coupling constant was not obtained due to second order character or complexity of the signal. [b] Not applicable due to a non- hydrogen substituent. [c] Chemical shift estimated from COSY spectrum.

dimethylcycloheptadienyl complex **138**, in contrast to results in the $C_5Me_5$ series, is formed in very low yield using this methodology.

The 1,7,7-trimethylcycloheptadienyl complex **139** is particularly interesting, as it demonstrates that even relatively unstable allyl complexes may be generated and trapped by acetylene to form seven-membered rings. The trimethyl complex **139** is also unique in that it is the only complex synthesized with two substituents on the $C_7$ position, except for the trace of spirocyclic cycloheptadienyl complex **120**. Data from the $^1H$ NMR spectrum show only two upfield signals, for $H_{6endo}$ ($\delta$ 1.46) and $H_{6exo}$ ($\delta$ 0.11), which share a mutual coupling constant of 12.6 Hz. Further confirmation that this is a geminal pair of hydrogen atoms is supplied by the HMQC spectrum, which indicates that these two hydrogen atoms are attached to the same carbon at $\delta$ 40.7 ($C_6$). The $^1J_{CH}$ value for this carbon is 130 Hz. The two $H_6$ hydrogens show further coupling to $\delta$ 5.13 ($H_5$), with $J$ values of 8.4 Hz ($J_{5\text{-}6endo}$) and 5.4 Hz ($J_{5\text{-}6exo}$). The $H_5$ signal is shown by homonuclear decoupling and COSY experiments to be adjacent to a signal at $\delta$ 6.15 ($H_4$) by a 6.6 Hz coupling constant. The $H_4$ signal is connected to $H_3$ ($\delta$ 7.29) by a coupling constant of 5.3 Hz. The assignment of $\delta$ 7.29 as the $H_3$ signal is further supported by the HMQC spectrum, which correlates this signal to the $C_3$ carbon signal at $\delta$ 98.2 ($^1J_{CH}$ = 174 Hz). Both the $H_3$ proton and $C_3$ carbon signals are the furthest downfield signals in their respective spectra, following the generalization that the $H_3$ and $C_3$ signals are the most deshielded signals in these seven-membered ring cobalt complexes. The $H_3$ signal is also connected to the last downfield signal, a doublet ($J$ = 6.8 Hz) at $\delta$ 5.26, assigned to $H_2$. The last two positions on the ring are fully substituted with methyl groups; thus, the proton spectrum is of little use for these assignments. However, there are three large (3H) singlets at 1.87, 1.81, and 0.92 ppm, assigned to the $C_1$ and the two $C_7$ methyl groups. The $^{13}C$ NMR spectrum shows two quaternary signals, one at $\delta$ 116.3, consistent with a coordinated quaternary $sp^2$ carbon, the other at $\delta$ 56.1, consistent with a tetrasubstituted $sp^3$ carbon. Both of these signals appear as singlets in the gated decoupled spectrum. The cyclopentadienyl ligand is identified by both the singlet at 5.52 ppm in the $^1$H NMR spectrum as well as the doublet ($^1J_{CH}$ = 184 Hz) at 98.2 ppm in the $^{13}$C spectrum. These two signals are correlated in the HMQC spectrum. We have observed that cyclopentadienyl ligands in these complexes typically have large values (180-185 Hz) for the $^1J_{CH}$ coupling constant, a fact that will become essential to subsequent compound characterizations.

Although only a low yield of the dimethylcycloheptadienyl complex **138** is obtained using this method, the preparation of complex **138** in higher yield is readily carried out by allowing silver tetrafluoroborate to react with the dimethylallyl bromide complex **140** in the presence of acetylene (Eq. **53**). The bromide complex **140** is formed in low (27%) yield by careful protonation of the isoprene complex **136** by HBr in THF at low temperatures.

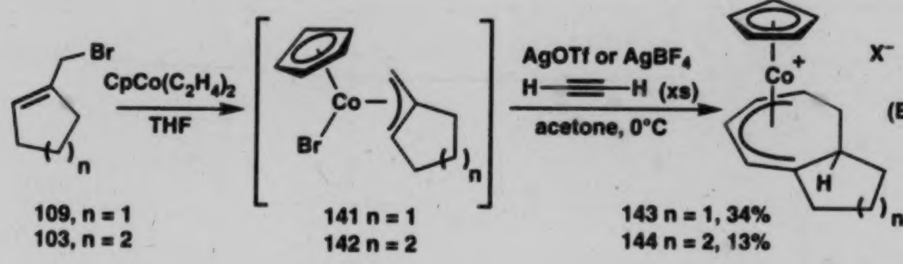


(Eq. 53)

The $^1$H NMR spectrum of complex **138** shows four downfield signals (7.18 (H$_3$), 5.67 (H$_4$), 5.55 (H$_2$) and 5.28 (H$_5$) ppm) that are consistent with a methyl-substituted pentadienyl fragment. The signal at δ 5.55 (H$_2$) is a simple doublet ($J$ = 7 Hz), suggesting it is adjacent to the methyl group. Using the COSY spectrum, the rest of the framework can then be assigned. This spectrum also shows a correlation between δ 5.28 (H$_5$) and two signals at δ 2.06 (H$_{6endo}$) and δ 1.15 (H$_{6endo}$). These two signals share a 15 Hz coupling, strongly indicating they are a geminal pair. The last ring hydrogen is assigned to a multiplet at δ 1.45 that is coupled to a methyl doublet at δ 1.37. The remaining methyl singlet resonates at 1.77 ppm, a chemical shift that suggests the methyl is attached to a sp$^2$ hybridized carbon atom.

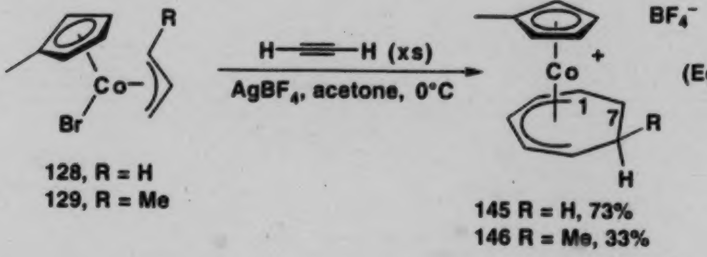
It is unclear why the dimethylcycloheptadienyl complex **138** is only formed in good yield by ionization of the allyl bromide complex **140** and not by $HBF_4$ protonation of the isoprene complex **136**. One possible explanation is that the dimethylallyl intermediate complex is unusually unstable; without additional stabilization provided by the strongly coordinating bromide or stabilization by acetone solvation, decomposition is faster than acetylene coordination. Thus, in dichloromethane, the dimethylallyl complex formed by protonation of the isoprene complex **136** lacks sufficient stabilization and decomposes prior to acetylene coordination. This explanation, however, does not rationalize the successful formation of the trimethylcycloheptadienyl complex **139** obtained from protonation of the 2,3-dimethylbutadiene complex **137**.

Almost all of the cyclopentadienyl [3 + 2 + 2] cycloaddition chemistry using cyclic allyl templates and acetylene directly correlates with the previously discussed pentamethylcyclopentadienyl examples (Eq. **54**). Bicyclic cycloheptadienyl analogues **143** and **144** are thus formed by allowing exocyclic allyl complexes **141** and **142** to react with acetylene, although lower yields are obtained compared to the reactions of pentamethylcyclopentadienyl complexes **103** and **111**. Nonetheless, extensive 2D NMR spectroscopy indicates that the overall structures of the $C_5H_5$ complexes are the same as their $C_5Me_5$ analogues.



(Eq. 54)

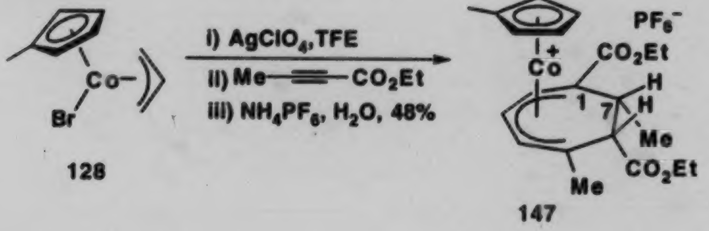
It was hoped that a methylcyclopentadienyl ligand, also readily available, would show greater similarity to the $C_5Me_5$ template than does the $C_5H_5$ analogue. The methyl group adds slightly more electron density to the ligand, yet still avoids the steric hindrance problem associated with larger ligands. The reactions of methylcyclopentadienyl cobalt allyl and crotyl complexes **128** and **129** with acetylene (Eq. **55**) parallel those of the $C_5Me_5$ complexes, forming cycloheptadienyl complex **145** and methylcycloheptadienyl complex **146** in low to moderate (33-73%) yields.



R
Co
Br
H—≡—H (xs)
AgBF₄, acetone, 0°C
BF₄⁻
Co
+
1
7
R
H
128, R = H
129, R = Me
145 R = H, 73%
146 R = Me, 33%

(Eq. 55)

The methylcyclopentadienyl template, however, undergoes one [3 + 2 + 2] reaction that bears more elaborate discussion. The reaction of allyl complex **128** with ethyl tetrolate (ethyl 2-butynoate) in trifluoroethanol with the addition of a silver salt gives a compound characterized as cycloheptadienyl complex **147**, isolated in 48% yield by flash chromatography (Eq. **56**). It is interesting to note that this is the only template that gives a tractable organometallic product using such an electron poor alkyne. It is uncertain what effects are present that permit this reaction to occur, when similar reactions fail using the $C_5Me_5$ or $C_5H_5$ allyl complexes **80** and **147**. Although fully characterized spectroscopically, the deep red oily product could not be isolated in analytical purity.



Co
Br
128
i) AgClO₄,TFE
ii) Me—≡—CO₂Et
iii) NH₄PF₆, H₂O, 48%
PF₆⁻
CO₂Et
Co
+
H
H
1
7
Me
CO₂Et
Me
147

(Eq. 56)

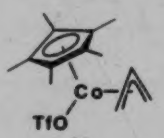
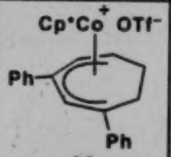
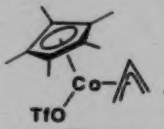
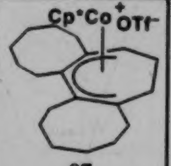
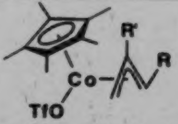
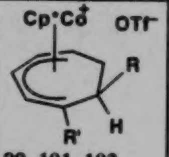
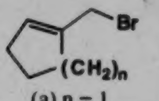
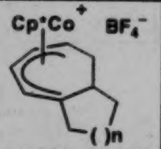
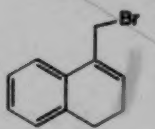
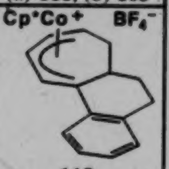
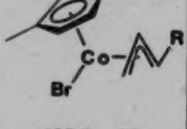
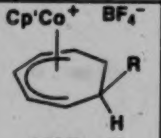
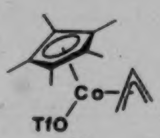
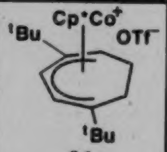
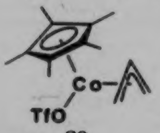
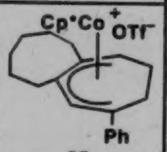
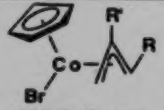
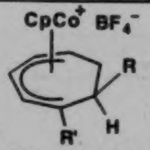
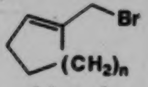
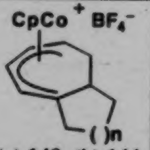
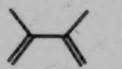
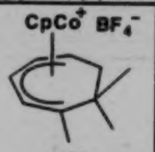
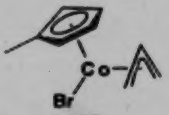
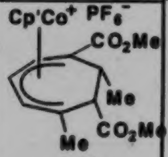
The methylcyclopentadienyl ligand of **147** is readily identified by four broad singlets in the $^1H$ NMR spectrum at 5.62, 5.54, 5.28 and 5.21 ppm, as well as a methyl singlet at δ 2.05. The downfield signals are correlated to carbon signals at 90.9, 90.6, 89.9 and 88.8 ppm, all of which all show $^1J_{CH}$ values of 180-186 Hz. The methyl signal is correlated to a carbon that resonates at 12.0 ppm and has a $^1J_{CH}$ of 130 Hz. The remaining quaternary carbon is located at δ 107.3.

The cycloheptadienyl ligand is readily identified by an upfield AMX pattern for the coordinated pentadienyl fragment. This consists of a signal at δ 7.46 assigned to the central hydrogen of the pentadienyl fragment ($H_3$), which shows coupling to two doublets at δ 6.38 ($J$ = 6.9 Hz, $H_2$) and δ 5.98 ($J$ = 7.2 Hz, $H_4$). The HMQC spectrum correlates these proton signals to carbon signal at δ 98.0 ($C_2$), 98.8 ($C_3$) and 94.8 ($C_4$). Two other quaternary carbon signals, 85.7 ($C_1$) and 105.8 ($C_5$) ppm, are assigned to the pentadienyl portion of the cycloheptadienyl ligand. From these data, the HMBC spectrum is used to determine the substituents on the terminal positions of the pentadienyl. A correlation between the $C_4$ signal at 98.0 ppm and a methyl group at 2.00 ppm in the $^1$H NMR spectrum indicates the presence of a methyl substituent at the $C_5$ position. Assignment of the $C_1$ substituent as an ester group is shown by a correlation between $H_2$ (δ 6.38) and a carbonyl carbon at δ 170.8 ($C_8$). Further correlations between $C_4$ and $H_6$ (δ 3.97) as well as between $C_2$ and $H_7$ (δ 3.54) are used with data from the HMQC spectrum ($H_6$ is attached to $C_6$ at 61.9 ppm and $H_7$ is attached to $C_7$ at 37.7 ppm) to fully assign the ring carbon atoms. The substituents on the sp$^2$ hybridized $C_6$ and $C_7$ atoms are an ester group and a methyl group respectively. Using the COSY spectrum, $H_7$ is seen to be coupled to the methyl group at δ 0.40 and using the HMQC spectrum, a correlation between the other carbonyl carbon (δ 167.3, $C_{12}$) and $H_6$ (δ 3.97) establishes the ester substituent at $C_6$.

The positions of the substituents on compound **147** provide evidence of an extensive series of β-H elimination/reinsertion reactions to form the observed pentadienyl fragment, far more than any other [3 + 2 + 2] cycloaddition product in cobalt, with the exception of the parent unsubstituted system **97** (*vide infra*). Part of the driving force for this rearrangement could be to achieve steric relaxation of the four buttressed substituent groups in the initial $\eta^1$-$\eta^4$-intermediate. In moving the two groups to *exo* positions on $sp^3$-hybridized carbon atoms, significant steric stress is alleviated. Electronic effects may also play a role in this rearrangement; conjugation of the pentadienyl $\pi$-system with the ester presumably stabilizes the system. In general, an electron withdrawing substituent on the $\alpha$-carbon stabilizes the metal-carbon bond.

Several cobalt templates with different cyclopentadienyl ligands have thus been shown to participate in [3 + 2 + 2] allyl/alkyne cycloaddition reactions. Table 4 gives a brief summary of the various $\eta^5$-cycloheptadienyl products obtained from this process.

**Table 4.** $\eta^5$-Cycloheptadienyl Complexes Obtained from [3 + 2 + 2] Allyl/Alkyne Cycloaddition Reactions

| allyl complex/ precursor | alkyne/ method/ yield | product |
|---|---|---|
|  **80** | PhCCH<br>A<br>59% |  **95** |
|  **80** | $C_8H_{12}$<br>A<br>84% |  **97** |
|  **80** R, R' = H<br>**81** R, R' = Me, H<br>**85** R, R' = Me | HCCH<br>A<br>(a) 52%<br>(b) 79%<br>(c) 80% |  **99, 101, 102** |
|  (a) n = 1<br>(b) n = 2 | HCCH<br>C<br>(a) 47%<br>(b) 59% |  (a) **111**, (b) **105** |
|  | HCCH<br>C<br>44% |  **118** |
|  **128** R = H<br>**129** R = Me | HCCH<br>C<br>(a) 73%<br>(b) 33% |  **145** R = H<br>**146** R = Me |
|  **80** | ${}^tBuCCH$<br>A<br>88% |  **96** |
|  **80** | $C_8H_{12}$/<br>PhCCH<br>B<br>63% |  **98** |
|  **125** R, R' = H<br>**126** R, R' = Me, H<br>**141** R, R' = Me | HCCH<br>C<br>(a) 47%<br>(b) 69%<br>(c) 58% |  **133, 134, 138** |
|  (a) n = 1<br>(b) n = 2 | HCCH<br>C<br>(a) 34%<br>(b) 13% |  (a) **143**, (b) **144** |
|  | HCCH<br>D<br>30% |  **139** |
|  **128** | MeCC-<br>$CO_2Et$<br>E<br>48% |  **147** |

**Conditions: A: $CH_2Cl_2$, excess alkyne, -78°C→RT, 12h. B: 1 equiv cyclooctyne, -30°C, 1 min, then PhCCH (1-2equiv), -30°C→RT, 12h. C: (i) $C_5R_5Co(C_2H_4)_2$, THF, 0°C→RT, 12h. ii) $AgBF_4$, acetone, 0°C, 30 min. D: $CpCo(C_2H_4)_2$, $CH_2Cl_2$, RT, 30 min, then $HBF_4$, xs alkyne. E: $AgClO_4$, xs alkyne, TFE, RT, 12h.**

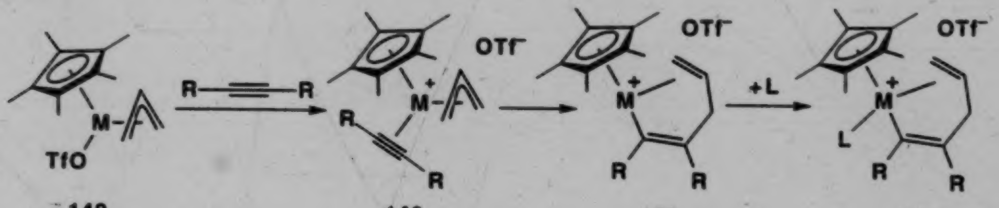
## *C. Mechanistic Proposals for [3 + 2 + 2] Cycloaddition Reactions*

### *1. Initial Allyl/Alkyne Coupling*

There is now ample evidence to support the initial step of the formal [3 + 2 + 2] cycloaddition pathway as the formation of an $\eta^2$-alkyne complex. The coordination of alkyne to form cobalt allyl/alkyne complexes has been observed spectroscopically by Etkin;[88] even more compelling evidence is the isolation of allyl/alkyne complexes of iridium (**38** and **45**) and ruthenium.[61,76,91] The iridium allyl/alkyne complexes are highly reactive and readily form seven-membered ring systems when allowed to react with excess alkyne in polar non-coordinating solvents such as dichloromethane. Electronic effects are also operative; in the Rubezhov and Schwiebert systems, as well as the cobalt templates, no tractable products are found using more electron deficient alkynes, such as DMAD. It is likely that the alkyne is simply too electron poor to coordinate at all, inhibiting the reaction. The coordination of the alkyne also appears to be relatively weak and reversible; Schwiebert has observed substantial amounts of a carbonyl complex formed from alkyne displacement by CO in the allyl/alkyne complex during trapping experiments. Rubezhov reports that no evidence of alkyne coordination is seen in coordinating solvents like DMSO or acetonitrile.[83]

Insertion of the allyl into the alkyne in allyl/alkyne complexes **149** provides a vinyl olefin complex, **150**, for which extensive corroborating evidence has also been gathered. Schwiebert has isolated vinyl olefin carbonyl complexes **151** (M = Ir, L = CO) from the reaction of allyl/alkyne complexes **38** (R = Me) and **45** (R = Ph) with carbon monoxide (Scheme **23**), although competitive displacement of the alkyne in **149** by CO is also observed. These vinyl olefin carbonyl complexes are also shown to provide competent intermediates in the formation of both five- and seven-membered ring products upon CO decomplexation. The reaction of an iridium complex (*e.g.*, **45**) with trimethylamine-N-oxide in the presence of excess alkyne forms seven-membered ring products; without added alkyne, a diphenylcyclopentadienyl complex is formed (Scheme **11**, p 32). However, there are several possible mechanistic routes that accomplish the latter transformation and more than one may be in operation.

**Scheme 23**

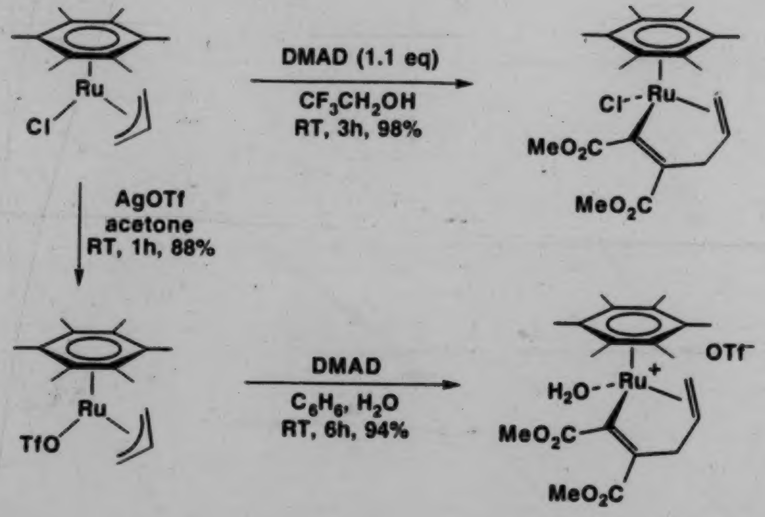


148 149 150 151

The allyl ligand may isomerize to an $\eta^1$ structure prior to migration onto the alkyne, as presumed by several workers who have observed alkyne insertion into $\eta^3$-allyl ligands, although no evidence for this isomerization is presented.[64,78,80,82-86] Similarily, the $\eta^3$-*syn-exo*-structure of all cobalt allyl complexes appears to be static by $^1$H NMR spectroscopy: no fluxionality or syn-anti interconversions are observed. Perhaps the $\eta^1$-allyl is only accessible as a transition state from the allyl/alkyne complex. The alkyne might first change from a two electron donor to a four electron donor, driving the allyl into the $\eta^1$-configuration. Only then does the $\eta^1$-allyl migrate to the alkyne ligand to form the vinyl olefin intermediate. However, it may equally be possible that an $\eta^1,\eta^2$-allyl migrates, keeping the relative stereochemistry intact throughout the process.

Further compelling evidence for the formation of vinyl olefin intermediates is seen in ruthenium chemistry from this group.[120] The reaction of ($\eta^6$-$C_6Me_6$)Ru($\eta^3$-$C_3H_5$)Cl with dimethylacetylenedicarboxylate forms a vinyl olefin complex in high yield (Scheme **24**). A similar complex can be obtained from the reaction of ($\eta^6$-$C_6Me_6$)Ru($\eta^3$-$C_3H_5$)OTf with DMAD in wet solvent (Scheme **24**).

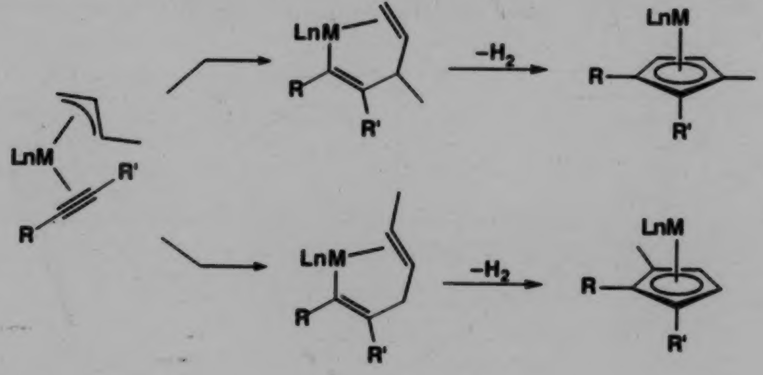
Scheme 24



DMAD (1.1 eq)
CF3CH2OH
RT, 3h, 98%
AgOTf
acetone
RT, 1h, 88%
DMAD
C6H6, H2O
RT, 6h, 94%
Ru
Cl
TfO
Cl- - Ru
MeO2C
MeO2C
H2O- - Ru+
OTf-

In theory, the migratory insertion of the allyl ligand into the metal-alkyne bond can proceed at either end of the allyl ligand. With crotyl complexes, however, the two ends of the allyl are dissimilar, thus the insertion reaction can potentially form two different vinyl olefin complexes (Figure **8**). To date, no conclusive evidence has been gathered to determine whether there is a preference for insertion into the less substituted side of a crotyl ligand in the cobalt templates, although this is the more likely site of reaction, due to fewer steric interactions. This is a difficult process to observe, as

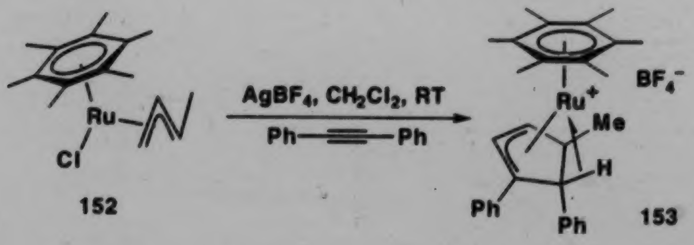
**Figure 8**. Regioisomers Formed From Crotyl/Alkyne Cycloaddition Reactions



LnM
R'
R
LnM
R
R'
-H2
LnM
R
R'
LnM
R
R'
-H2
LnM
R
R'

enantiomeric products are obtained from the insertion of symmetrical alkynes at either end of the crotyl ligand (Figure **8**). In both five- and seven-membered ring products, the only consequence of insertion of a symmetric alkyne to opposite ends of the crotyl is the formation of enantiomeric products. Presumably, an unsymmetrical alkyne could be used to distinguish which end of the crotyl is active in the insertion reactions, although this has not been fully established. However, the alkyne may also have a preferred insertion geometry, which further complicates the interpretation of this reaction. Although Etkin observes a mixture of cycloheptadienyl complexes in a reaction between Cp*Co(crotyl) complex **81** and *t*-butylacetylene in dichloromethane, small amounts of a cobalticenium product are also observed. However, the exact substitution pattern of neither the cyclopentadienyl product nor the seven-membered rings was firmly established.[88] The seven membered ring systems in particular did not appear to have a straightforward pattern; this product will be discussed in more detail in the following chapter. All other reactions of cobalt crotyl complex **81** used symmetrical alkynes, thus the regiochemistry of the insertion process cannot be determined.

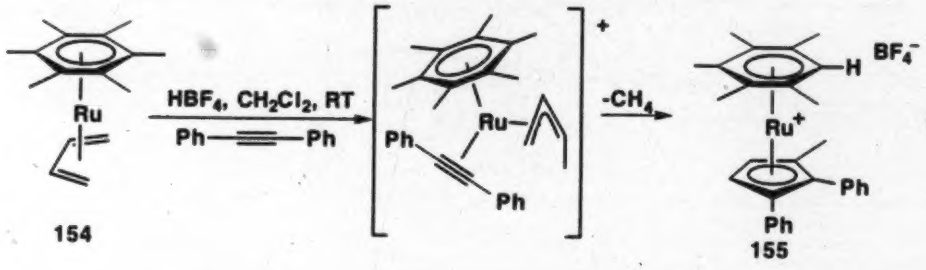
Migration of the *syn exo* crotyl ligand onto the alkyne is predicted to place the methyl group *endo* to the cobalt center. This has several consequences for later rearrangements by preventing facile β-H elimination reactions on the carbon center bearing the *endo* methyl group. In a related ruthenium system (Eqs. **57**, **58**), widely different products are obtained when an alkyne is allowed to react with *syn* or *anti exo* crotyl complexes .[120] The reaction of the *syn* crotyl chloride complex **152** with silver tetrafluoroborate and diphenylacetylene (Eq. **57**) yields the agostic cyclopentenyl



**152** **153** (Eq. 57)

complex **153**. This complex is stable to further rearrangement as the *endo* methyl group prevents β-hydrogen elimination reactions from a diene intermediate.

Protonation of butadiene complex **154** yields an *anti* crotyl intermediate complex; when this reaction is run in the presence of diphenylacetylene, cyclopentadienyl complex **155** is formed exclusively (Eq. **58**). In this reaction, cyclization forms a cyclopentenyl complex with an *exo* methyl group. The methyl does not prevent β-hydride elimination and thus does not prevent aromatization to the cyclopentadienyl ring.



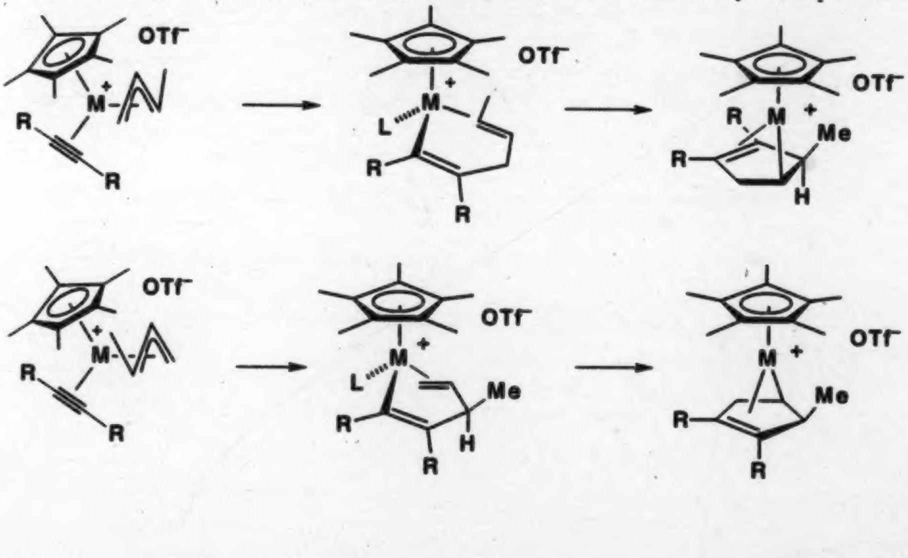
154

155

(Eq. 58)

The same stereochemistry is expected in the closure to form seven-membered rings, thus the *syn* crotyl ligand forms a cycloheptadienyl complex with an *endo* methyl group. As seen in Figure **9**, insertion into either end of the crotyl ligand is expected to form an *endo* methyl group. As this stereochemistry is determined at the first insertion,

**Figure 9**. Product Stereochemistry of Alkyne Insertion into Crotyl Complexes

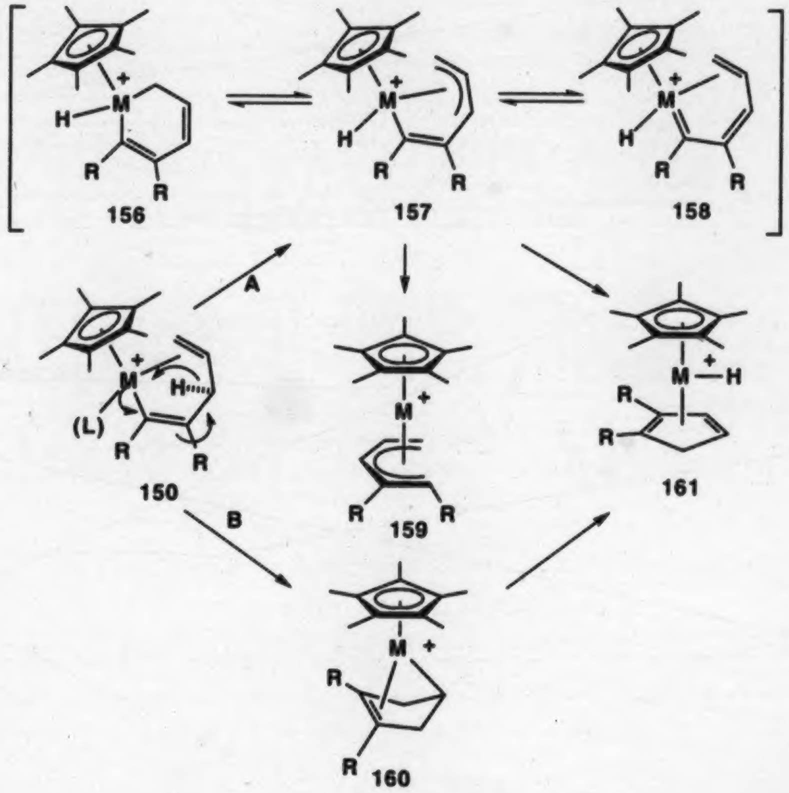


both five- and seven-membered ring products formed from crotyl complexes are expected to have an *endo* methyl substituent. However, in contrast to the above ruthenium example, the cobalt template appears to readily eliminate dihydrogen to produce cyclopentadienyl ligands, even with the *endo* methyl group.

### 2. *[3 + 2] Cyclization Steps*

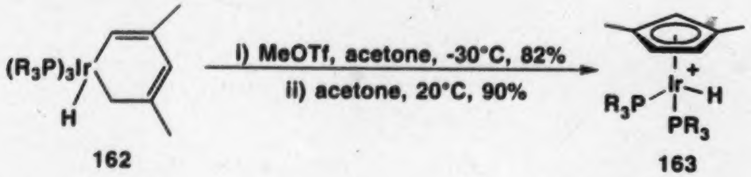
Although the carbonyl vinyl olefin complexes **73** and **76** (*cf.*, **151**, Scheme **23**) are stable, decarbonylation reforms a highly reactive unsaturated vinyl olefin intermediate **150** (Scheme **25**). This likely receives additional stabilization through the coordination of

**Scheme 25**



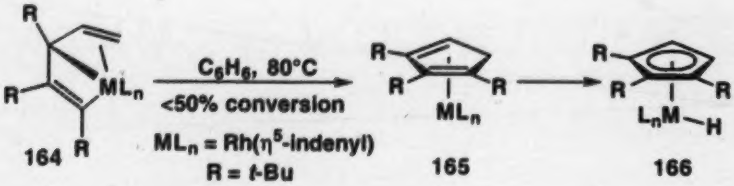
solvent, triflate, additional alkyne, or by the formation of an $\eta^2$-vinyl ligand, if the metal orbitals are suitably oriented. This intermediate may not always cyclize, as seen in related ruthenium chemistry from this research group, in which acyclic pentadienyl complexes are formed (Scheme **25**).[120] This presumably occurs by activation of the allylic hydrogen. There are numerous potential approaches to this process and several different bonding arrangements for the intermediates; however, only an illustrative few are discussed. The direct product of carbon-hydrogen activation (**157**) appears to have an unfavorable geometric arrangement of the ligand but the $\eta^1$-allyl form (**156**) should be more favorable geometrically, although this is formally a 16-electron intermediate. A further bonding picture can be envisioned if these formally Co(V) structures relax into a Co(III) carbene structure. This structure is also available via a concerted hydrogen atom abstraction from **150** assisted by electron donation from the metal-vinyl, in a five-centered transtion state. Here, a metal-carbon bond to the central carbon never needs to be proposed, avoiding what would be a geometrically strained arrangement and the abnormally high Co(V) oxidation state is avoided.

The intermediate structures **156-158** are all able to rearrange to the open pentadienyl complex **159** by reductive elimination or 1,2-hydride migration. In addition to the hydride rearrangements, a rearrangement of the carbon skeleton of the ligand is also feasible. In most systems and in the absence of excess alkyne, intermediate **150** is transformed into a cyclopentadienyl ligand by cyclization and the loss of two hydrogen atoms. Several alternate pathways may again operate (Scheme **25**). A common intermediate on these pathways is the cyclopentadienyl hydride structure **161**. One route to **161** (Path A) can proceed by the previously proposed C-H activation of the allylic hydrogen, similar to the process of pentadienyl formation. The metallacyclohexadiene hydride **156** can undergo reductive elimination to **161**. This latter process has been demonstrated by Bleeke in an iridium system (Eq. **59**), in which reductive elimination presumably forms an intermediate cyclopentadiene complex, which undergoes C-H activation to form the cyclopentadienyl hydride product **163**.[121] Methyl triflate is used to induce coordinative unsaturation by abstracting the metal hydride from iridacyclohexadiene **162**, releasing methane in the process.



(Eq. 59)

A second possibility for the cyclization mechanism is the migration of the vinyl to the olefin (Path **B**, Scheme **25**) to directly form nonconjugated $\eta^1$-$\eta^2$-cyclopentenyl complex **160**, which may undergo facile β-hydrogen elimination to form cyclopentadiene hydride **161**. This process seems to be the most likely possibility for the cyclization process, as other intermediates appear to be either high energy or unnaturally high oxidation state complexes. Note that the pendant olefin must be bent off axis to allow the vinyl to reach the olefin and migrate. A similar migratory rearrangement has been seen by Hughes in iridium and rhodium systems (Eq. **60**), although no greater mechanistic detail is available from those results.[122] An analogous vinyl migration process is also thought to occur in the cyclization to form six- or seven-membered carbocyclic products (*vide infra*).

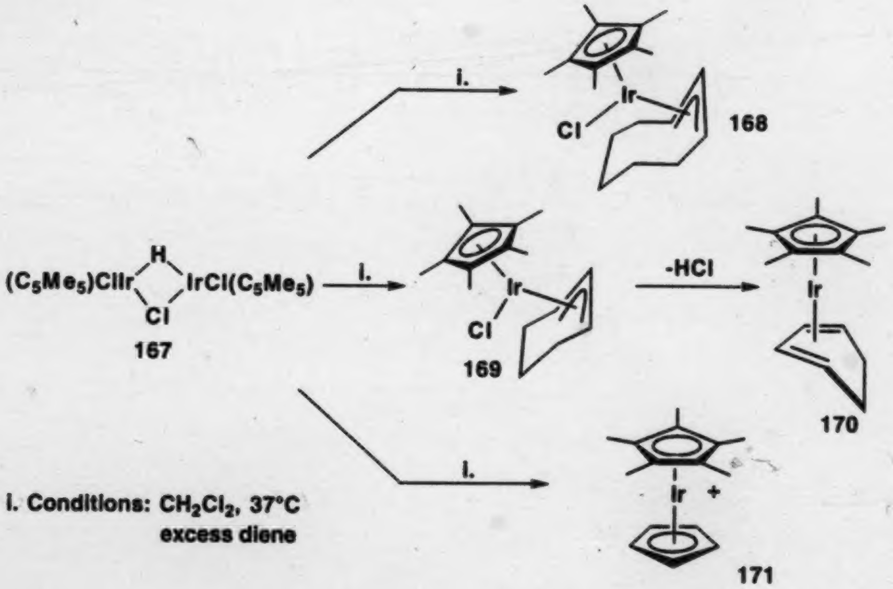


(Eq. 60)

### 3. *Loss of Hydrogen From the Cyclized Product*

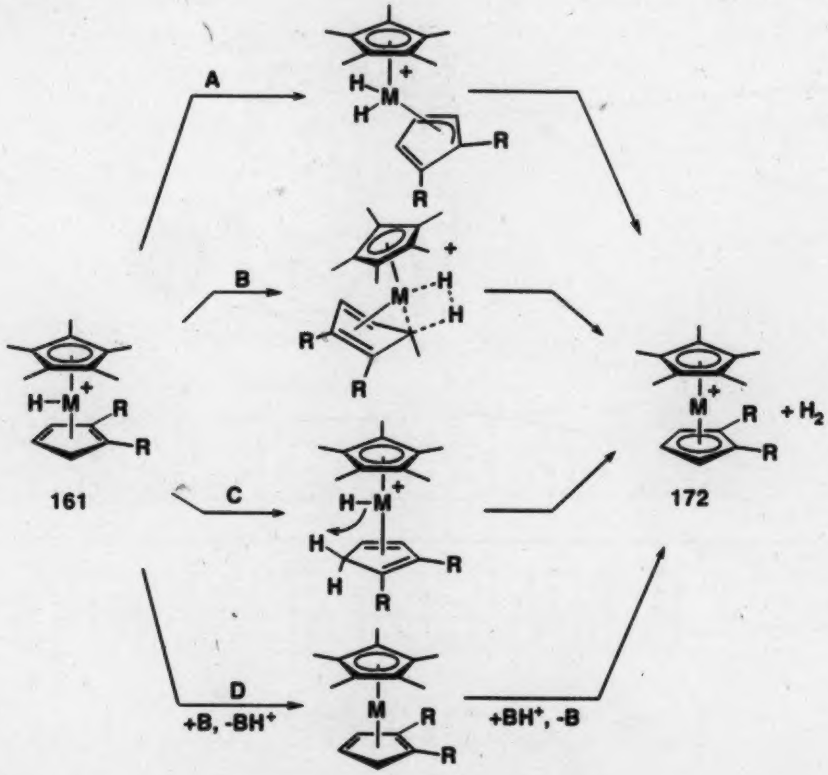
The exact mechanism of hydrogen loss from the cyclopentadienyl hydride to form cyclopentadienyl complexes is still speculative. Although no detailed mechanistic study was undertaken, Rubezhov reported the detection of dihydrogen and stilbene byproducts during the production of cyclopentadienyl products from allyl complexes and diphenylacetylene.[83] Several other examples of hydrogen loss or transfer from cyclopentenyl or cyclopentadiene complexes are known. The reaction of cyclopentenylmagnesium bromide with nickel(II) bromide generates ($\eta^5$-cyclopentadienyl)($\eta^3$-cyclopentenyl)nickel exclusively; the expected bis($\eta^5$-cyclopentenyl)nickel was not detected.[123] Maitlis reports that reaction of metal hydride complexes **167** with dienes generally yield cycloalkenyl complexes, such as the cyclooctenyl complex **168** (Scheme **26**).[124] However, the reaction of **167** with cyclopentadiene does not give the expected cyclopentenyl product but rather the cyclopentadienyl complex **171**, with loss of two hydrogen atoms. The reaction of the hydrido dimer **167** with cyclohexadiene initially forms an observed but unstable cyclohexenyl complex (**169**), which eliminates HCl to form the diene complex **170**. Similar results are seen in the reaction of $[Cp^*MCl_2]_2$ (M = Rh, Ir) with $Na_2CO_3$ and cycloalkadiene in ethanol solvent.[125]

**Scheme 26**



Although many examples of reactions in which two hydrogen atoms are lost from a cyclopentenyl ligand to form a cyclopentadienyl complex are known, there is no single proven mechanism. Several possible processes (Scheme **27**) may be involved; perhaps the simplest is the formation a metal dihydride complex from allylic C-H activation of the ligated cyclopentadiene (Path **A,** Scheme **27**). Reductive elimination from the high oxidation state intermediate directly produces the metallicenium complex **172**, with the evolution of dihydrogen gas. Stable pentavalent rhodium and iridium hydride or polyhydride complexes are known,[126] thus lending support for the existence of such dihydride intermediates on the dehydrogenation pathway even in the case of cobalt. The same event is also achieved via a concerted extrusion of dihydrogen (Path **B**), similar to a σ-bond metathesis, directly producing the metallicenium cation from the hydrido

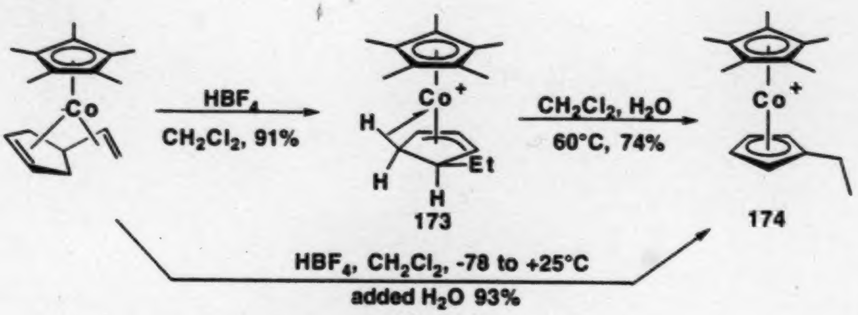
**Scheme 27**



cyclopentadiene complex **161**. A slight variation of the "nonpolarized" metathesis pathway is the direct attack of the metal hydride on the acidic hydrogen of the cyclopentadiene, either in an intermolecular or intramolecular process (Path **C**). The intramolecular process can also be viewed as a polarized version of path **B**. Although all of these processes are competent, one less complicated pathway may be in operation. Adventitious Lewis bases such as water, solvent, or even the triflate counterion may scavenge the metal hydride, leaving behind a neutral cyclopentadiene complex (Path **D**). Hydride may then directly be abstracted from the neutral cyclopentadiene complex by the protonated base. It is known that sulfuric acid protonation of cobalt cyclopentadiene compounds generates a cyclopentadienyl ligand with loss of dihydrogen gas; this is proposed by the authors to be a hydride abstraction.[127] Recent results in our laboratory suggest that this process is almost certainly occurring in related ruthenium systems.[120]

Another example of cyclopentadiene complex rearrangements is known in the literature. Vinylcyclopentene complexes of cobalt form thermally stable but fluxional agostic ethylcyclopentenyl complexes upon protonation by $HBF_4$ in dichloromethane solvent (Scheme **28**).[128] This agostic allyl complex can be deprotonated by added base (LDA) to give an ethylcyclopentadiene complex. Consistent with pathway **D** in Scheme **27**, Spencer reports that the agostic allyl complex **173** readily loses hydrogen in the presence of water to form ethylcyclopentadienyl complex **174**. It is interesting to note that once the agostic complex **173** is formed, it requires moderate heat (60°C) and several hours to convert to the cyclopentadienyl structure. In contrast, use of wet solvent in the initial reaction directly forms the yellow cobalticenium salt **174** at room temperature, suggesting that the agostic complexes may not be directly on the mechanistic pathway for hydrogen loss. Intermediate **173**, once formed, is apparently at an energy minimum and must first climb out of this well and become non-agostic before hydrogen loss can take place.

Scheme 28

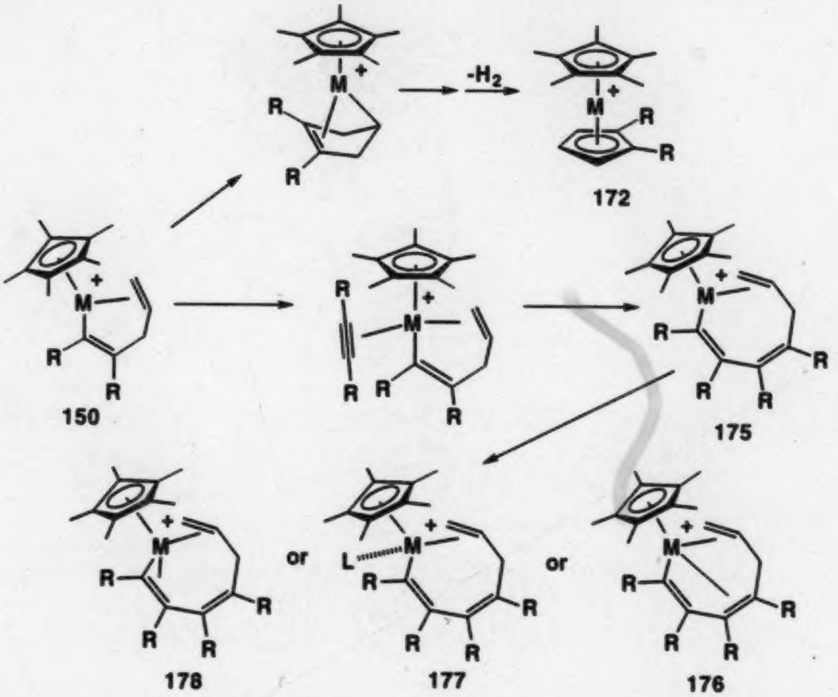


### *4. Double Alkyne Insertion*

Strong solvent effects are noted in the [3 + 2 + 2] allyl/alkyne cycloaddition pathway. Rubezhov reports that both [3 + 2] and [3 + 2 + 2] allyl/alkyne cycloaddition products are observed using acetone, a weakly coordinating solvent, but in dimethylsulfoxide or acetonitrile, even single alkyne insertion is not observed.[83] Presumably, like CO, these latter solvents are simply much stronger ligands than the alkyne and prevent coordination, "poisoning" the metal center. Coordination of the second alkyne is much more sensitive to solvent effects; Nehl reports only single insertion products in tetrahydrofuran solvent, even using a large excess of 2-butyne.[84,85] We have shown that utilization of dichloromethane in place of tetrahydrofuran gives a high yield of the double insertion product when allyl complex **80** reacts with 2-butyne and other alkynes. Work in this laboratory has also confirmed that tetrahydrofuran inhibits the second coordination of an alkyne.[88] The reactions of allyl complex **80** in tetrahydrofuran using various alkynes that otherwise show [3 + 2 + 2] activity give predominantly single alkyne insertion products. The partition between the two reaction manifolds is thus tremendously influenced by the choice of solvent; even a moderately coordinating solvent interferes with the coordination of the second alkyne, allowing cyclization to the five-membered ring product to kinetically predominate.

Other factors also affect the partition between single and double allyl/alkyne insertion products. As previously noted, the initial steps are assumed to be common for the two reaction pathways, but similarities end once the vinyl olefin intermediate is formed. If the rate of ring closure (or any other mechanistic event) is fast relative to coordination of the second alkyne (Scheme **29**), a large proportion of single insertion

**Scheme 29**

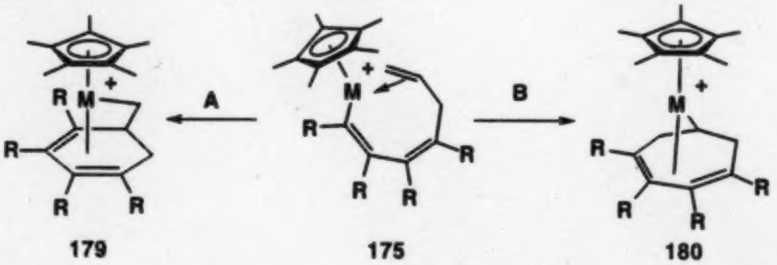


product is obtained; however, this may be inhibited by the coordination of another alkyne. Coordination of the second alkyne does not necessarily preclude migratory insertion closing to a five-membered ring. Insertion of this second alkyne into the vinyl olefin intermediate, however, leads to an unsaturated seven-carbon vinyl ligand containing a pendant olefin (**175**), similar to the process proposed for the initial allyl/alkyne insertion. Intermediate **175**, although possibly a 16 electron coordinatively unsaturated species, may be stabilized by the coordination of the internal olefin of the seven carbon ligand (**176**). Other available ligands include alkyne, solvent molecule and the triflate counterion (**177**). There is also a possibility for the formation of an $\eta^2$-vinyl species (**178**). Although there is no reason to suggest a third alkyne cannot coordinate, rearrangement of this intermediate must be fast compared to further insertion of the alkyne, as no alkyne oligomerization products have been isolated. Although the partitioning between single and double insertion products has not been studied mechanistically, one key feature is apparent. Larger cyclopentadienyl ligands as well as larger groups on the alkyne or allyl ligand all tend to hinder the approach of the second alkyne, thus favoring five-membered ring formation.

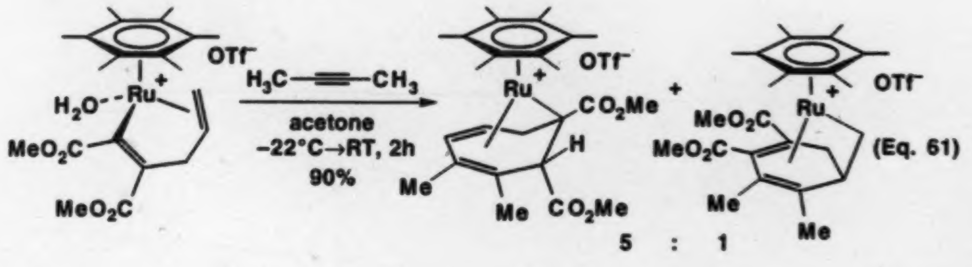
### *5. Cyclization of the Vinyl Diene*

The vinyl diene complex **175** formed from insertion of a second alkyne into the allyl ligand is presumed to be highly reactive and no spectroscopic evidence has been obtained for this intermediate. Furthermore, no indication of triple alkyne insertion products has been seen, suggesting that cyclization of this intermediate is fast relative to further alkyne coordination. This cyclization can potentially proceed via any of the pathways **C**, **D**, or **E** proposed for the five-membered ring synthesis (Scheme **25**, page 86); however, to account for the observed partitioning between six- and seven-membered rings, we propose that pathway **D**, the simple migratory insertion pathway, must operate. Migration of the vinyl group to the internal or terminal olefin carbon (Scheme **30**) forms

**Scheme 30**



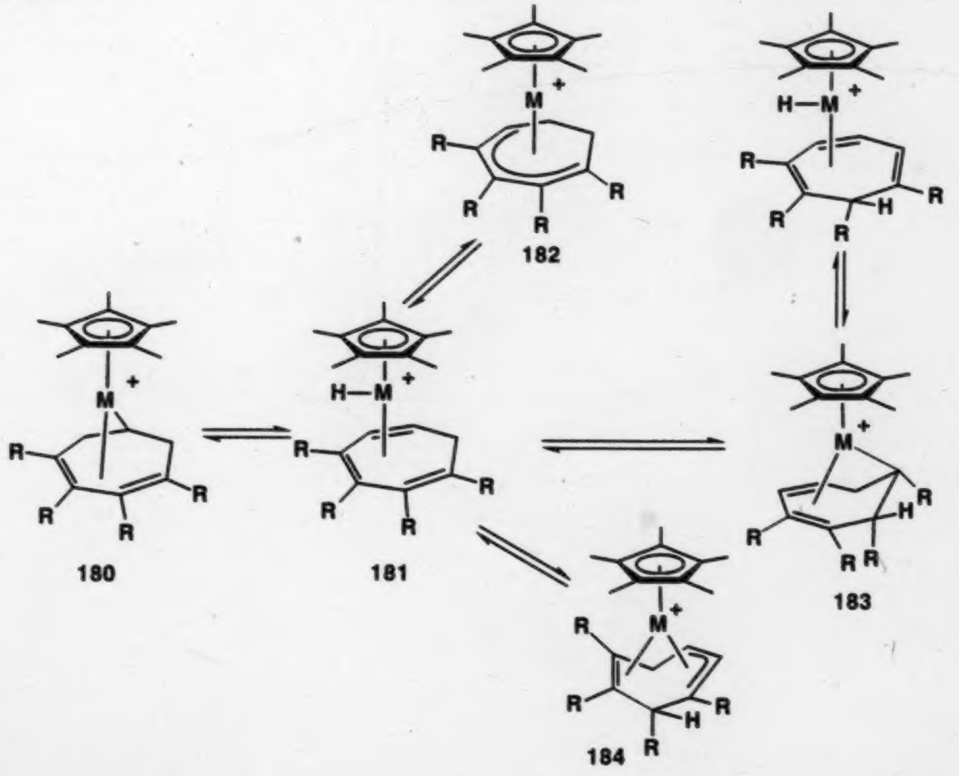
methanocyclohexadiene complex **179** or $\eta^1,\eta^4$-cycloheptadienyl complex **180**, respectively. There appears to be a marked steric effect of the cyclopentadienyl framework on this partition. The unsubstituted cyclopentadienyl or benzene metal complexes reported by Rubezhov show migration selectively to the internal carbon, forming the six-membered ring product. In contrast, however, Schwiebert's pentamethylcyclopentadienyliridium system produces mainly the seven-membered carbocycle, although a small amount of the six-membered ring analogous to that reported by Rubezhov is also seen. The steric effect of the ancillary ligand is also seen in ruthenium templates also investigated by our group: in the analogous ($\eta^6$-mesitylene)ruthenium vinyl olefin complex an approximately 1:1 selectivity for six- and seven-membered ring products in the reaction with alkyne is seen.[120] The $\eta^6$-hexamethylbenzene ruthenium analogue exhibits a 5:1 ratio favoring the seven-membered carbocycle (Eq. **61**).[120] Although many cyclizations in the ruthenium systems have been observed, a number of acyclic byproducts are also obtained, demonstrating that cyclization is not the only possible pathway for the seven-carbon vinyl olefin ligand. In the much smaller cobalt templates, both $C_5H_5$ and $C_5Me_5$ ancillary ligands apparently force migration to the olefin terminus, producing seven-membered ring products exclusively. No evidence for the formation of an $\eta^1,\eta^4$-methanocyclohexadiene product is seen in either cobalt system.



### ***6. Rearrangements of Seven-Membered Carbocycles***

The initial insertion product of the vinyl diene into the terminal position of the pendant olefin is the $\eta^1,\eta^4$-cycloheptadiene complex **180**. This complex can rearrange through a series of β-hydrogen elimination and reinsertion reactions. From the initially formed $\eta^1,\eta^4$-isomer, β-hydride elimination forms $\eta^4$-cycloheptatriene metal hydride **181** (Scheme **31**). Several pathways are available for further reactions; the hydride can, in principle, migrate to any of the coordinated carbons, forming three distinct coordination isomers, the $\eta^5$-dienyl (**182**), $\eta^1,\eta^4$-σ-diene(**183**) and $\eta^3,\eta^2$-allyl olefin (**184**) structures. Two of these (**182** and **183**) have been observed as products or intermediates in our laboratory (Scheme **31**). Larger ring systems ($C_8$ and larger) prepared through different

**Scheme 31**

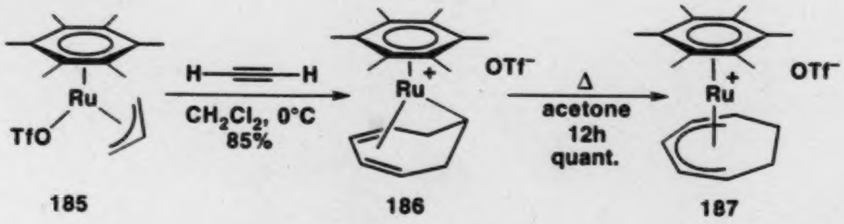


methodologies are known to support the $\eta^3,\eta^2$-allyl olefin structures.[129] The thermodynamic resting state of this process is highly metal-dependent, although in both iridium and cobalt systems, $\eta^5$-cycloheptadienyl complexes are isolated as the sole coordination isomer formed in seven-membered ring products. Schwiebert's pentamethylcyclopentadienyl iridium template generates different substitutional isomers, indicating that several β-hydride elimination/reinsertion steps have occurred, although no evidence for intermediate structures can be inferred from these data.[61,62] Isolated complexes obtained from mixtures of $\eta^5$-isomers show no tendency to interconvert thermally, suggesting that the formation of an $\eta^5$-cycloheptadienyl complex is irreversible. In the cobalt systems, the formation of cycloheptadienyl complex **147** from ethyl butynoate also indicates that extensive rearrangement can occur subsequent to cyclization. Ruthenium systems, in contrast, appear to prefer to form $\eta^1$-nonconjugated isomers such as **183**, although this is dependent on the nature of the substituents.[120]

Some ruthenium reactions show a strong preference for the $\eta^1$-$\eta^4$-cycloheptadienyl coordination isomer (*e.g.*, Eq. **61**). A reasonably wide range of alkynes undergo this cycloaddition reaction; in addition to 2-butyne, acetylene, cyclooctyne and DMAD all form similar products, although substitution pattern changes slightly when DMAD is used. Futhermore, several of these reactions are complicated by the formation of small amounts of byproducts.

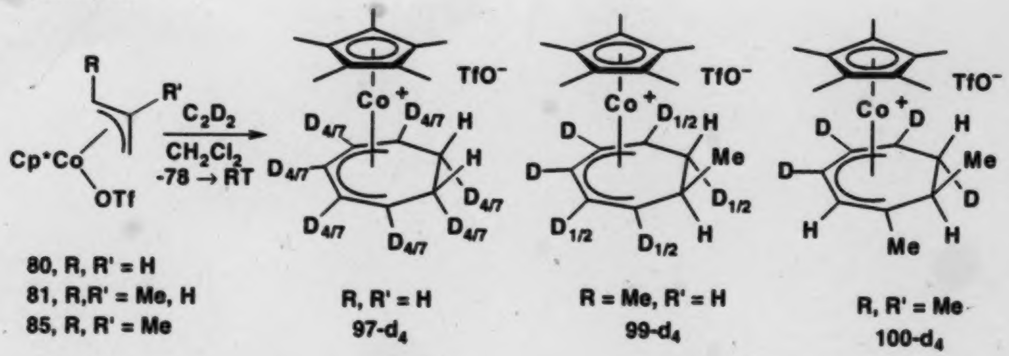
This interconversion has been demonstrated in a ruthenium system, where it has been shown that the $\eta^1,\eta^4$-cycloheptadienyl product (**186**), which is formed by a [3 + 2 + 2] cycloaddition reaction between acetylene and $\eta^6$-$C_6Me_6Ru(allyl)(OTf)$ (**185**), is the kinetic product (Scheme **32**).[120] Although most other ruthenium $\eta^1$-$\eta^4$-$\sigma$-diene complexes are inert up to decomposition temperatures, the rearrangement of **186** to $\eta^5$-cycloheptadienyl complex **187** occurs upon heating. In addition, the $\eta^1,\eta^4$-complex **186** is fluxional by $^1$H NMR spectroscopy at room temperature, consistent with a series of β-hydrogen elimination and reinsertion reactions.[120] Mild heating irreversibly forms the $\eta^5$-cycloheptadienyl isomer **187**, which has a static structure.

**Scheme 32**.


Ru
TfO
185
H—≡—H
$CH_2Cl_2$, 0°C
85%
Ru +
OTf⁻
186
Δ
acetone
12h
quant.
Ru +
OTf⁻
187

In order to gain further mechanistic insight into the acetylene insertion reactions in cobalt, a series of deuteration studies was undertaken, but the full implication of these data was not appreciated at the time.[88] When the parent allyl triflate complex **80** is permitted to react with acetylene-$d_2$, all positions in the resulting cycloheptadienyl complex **97**-$d_4$ except the $6_{endo}$ and $7_{endo}$ positions are partially and equivalently deuterated (Scheme **33**). Repetition of the deuteration experiment using the crotyl triflate complex **81** yields a more specifically deuterated product, but this product still exhibits partial scrambling. The product derived from the dimethylallyl complex **85** and acetylene-$d_2$ shows specific deuterium incorporation into the 1, 2, 3 and 7*exo* positions (**100**-$d_4$).

**Scheme 33**

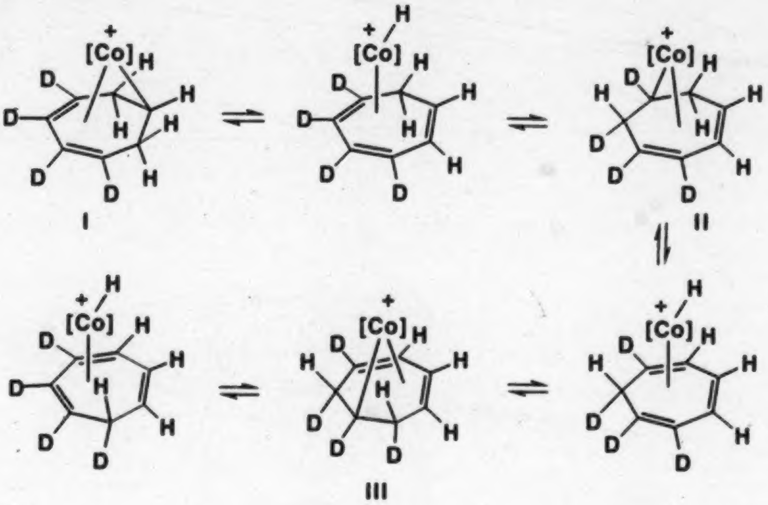

R
R'
Cp*Co
OTf
$C_2D_2$
$CH_2Cl_2$
-78 → RT
80, R, R' = H
81, R,R' = Me, H
85, R, R' = Me
Co +
TfO⁻
$D_{4/7}$
H
R, R' = H
97-$d_4$
Co +
TfO⁻
D
$D_{1/2}$
Me
H
R = Me, R' = H
99-$d_4$
Co +
TfO⁻
D
H
Me
R, R' = Me
100-$d_4$

In the unsubstituted case, only the *endo* H atoms are unscrambled, suggesting that a facile β-hydride elimination/reinsertion mechanism for deuterium scrambling exists.

The atom originally positioned for β-hydride elimination must be hydrogen, not deuterium. Since reinsertion places the hydride *endo* to the metal, only hydrides are available for elimination. Thus, the metal always picks up a hydride instead of a deuteride. One consistent rationale is that intermediates in the unsubstituted complexes are highly fluxional, forming all possible $\eta^1$,$\eta^4$-isomers from the triene hydride (**I**, **II**, **III**, Scheme **34**). This process is proposed to be rapid relative to irreversible formation of the $\eta^5$-isomer, thus permitting the unsubstituted compound to fully equilibrate. It was originally proposed that a series of $\eta^5$-cycloheptadienyl structures were formed from similar hydride shuttling; either process can account for the observed isomers. However, the high temperature $^1$H NMR spectrum (400 MHz, tetrachloroethane-$d_2$, 100°C) of the undeuterated complex **97** is identical with the static spectrum obtained at room temperature, indicating no fluxionality on the $^1$H NMR spectroscopic time scale. If the complex shows no evidence of fluxionality at 100°C, the $\eta^5$-structure formed at or below room temperature must be static and all the observed deuterium scrambling must occur before the final $\eta^5$-cycloheptadienyl structure is formed. This excludes the series of $\eta^5$-cycloheptadienyl-to-triene hydride equilibria as a viable mechanism, suggesting that the $\eta^1$,$\eta^4$-isomerization pathway operates, as seen in the ruthenium series.

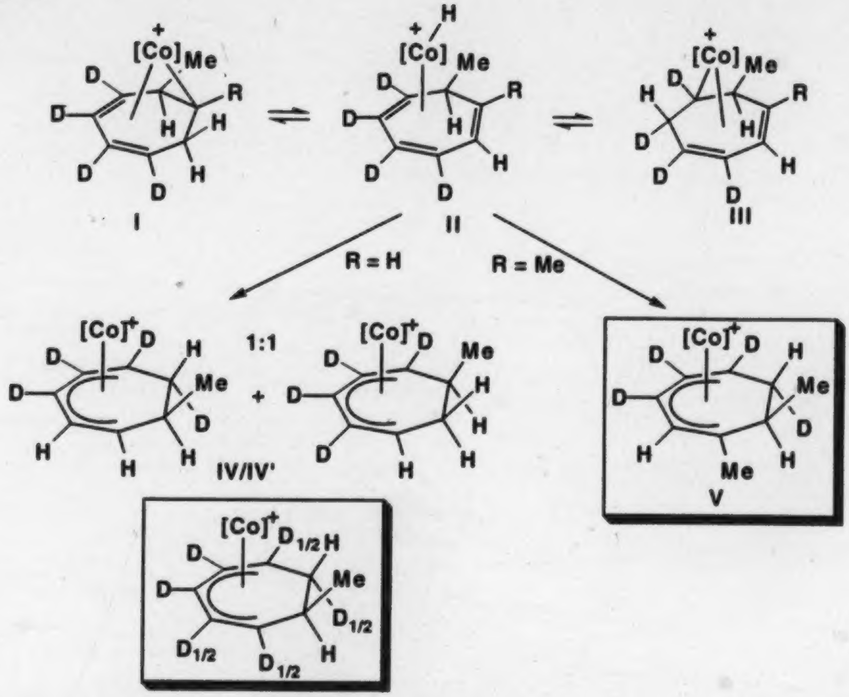
The unsubstituted complex **97** has no substituent barrier to β-hydride elimination; thus, all possible $\eta^1$, $\eta^4$-σ-diene structures are available, resulting in complete scrambling of the deuterium atoms over all positions except the $6_{endo}$ and $7_{endo}$ positions. In the initially formed σ-diene intermediate (Intermediate **I**, Scheme **34**), only hydrogen atoms are available for elimination and thus the *endo* positions always carry a hydride, as discussed above. Since the series of β-hydride eliminations and reinsertions are proposed to be fast relative to final conversion to the $\eta^5$-cycloheptadienyl product, all available positions are equivalently deuterated.

Scheme 34



The limited scrambling of deuterium observed in the substituted complexes is also readily explained. The *endo* methyl groups of complexes **99** and **100** prevent full scrambling of the deuterium label by blocking β-H elimination to that position, limiting the number of possible isomers. Thus, for **99** and **100**, the initial σ-diene cycloheptadienyl structure **I** (Scheme **35**) can only undergo a β-hydride elimination in one direction, forming triene hydride **II**; elimination in the opposite direction is blocked by the methyl group. The intermediate triene hydride complex can form another σ-diene isomer **III**, which is again blocked from additional β-hydride eliminations by the *endo* methyl group. Thus, only one triene hydride intermediate (**II**) can be accessed in this reaction manifold. Another general observation is that in the cobalt triene hydride intermediates, unlike the iridium triene hydrides, the hydride does not normally migrate to a substituted position. This explains the selective formation of a single isomer in complex **100**: the migration of the hydride onto the methyl group on the end of the triene is disfavored.

**Scheme 35**



For intermediate **II** (Scheme **35**) and R = H (complex **99**), there are two positions for the hydride to reinsert to form the cycloheptadienyl product, one on either side of the methyl group, resulting in two product structures (**IV** and **IV'**). However, these two compounds are enantiomeric and will have the same NMR spectral properties aside from the deuterium labels. The $^2$H NMR spectrum shows two large deuterium signals and four other signals that integrate to 1/2 deuterium each. Furthermore, the chemical shifts are consistent with the proposed structure. In the case where R = Me (Scheme **35**) and with the additional fact that the hydride migration on top of an alkyl group appears to be disfavored, only one $\eta^5$-cycloheptadienyl isomer **V** (R, R' = Me, **100**) can be produced in the final step, leaving the four deuterium atoms unscrambled. These deuterium labeling results are consistent only with the formulation of an *endo* methyl group, as the *exo* methyl would not be expected to interfere with full scrambling of the deuterium atoms in the intermediate complexes.

## III. Conclusions and Future Topics

The [3 + 2 + 2] cycloaddition reactions of $(\eta^5\text{-}C_5Me_5)Co(\eta^3\text{-}C_3H_5)(OTf)$ with some terminal alkynes has been shown to yield $\eta^5$-cycloheptadienyl complexes. However, the selection of alkynes is relatively limited; many alkynes give inseparable mixtures of isomeric cycloheptadienyl products or intractable material. Internal alkynes also show limited useful reactivity and on occassion (*e.g.*, using 2-butyne) extensively rearranged cycloheptadienyl products are formed (Chapter 4).

The somewhat unexpected reaction of this template with acetylene proved to be much more useful. Acetylene is an effective agent for [3 + 2 + 2] cycloaddition reactions using a variety of substituted allyl templates. This acetylene [3 + 2 + 2] cycloaddition reactivity pattern has also been demonstrated in the cyclopentadienylcobalt ligand system. The facile formation of bicyclic systems has been demonstrated in both templates by using exocyclic allyl complexes, which expands the synthetic possibilities for this reactivity pattern.

Development of more highly functionalized allyl ligands appears to be the most promising route for further applications to organic synthesis. An intramolecular version of this reaction is also of great interest; better control of the insertion chemistry may be possible. Unfortunately, the use of tethered allyl-alkyne substrates for intramolecular cycloaddition reactions has produced disappointing results thus far.[130] The use of allyl ligands with tethered pronucleophiles has recently been shown in our laboratory to produce cycloheptadienyl complexes from reaction with acetylene.[131] The reaction of a seven-membered ring complex that contains a tethered pronucleophile with base has provided a diene product tentatively identified as a bicyclic complex.[131] Further expansion of this reactivity pattern can potentially provide a variety of synthetically valuable bicyclic systems.

# Chapter 3. Functionalization and Demetallation of $\eta^5$-Cycloheptadienyl Complexes.

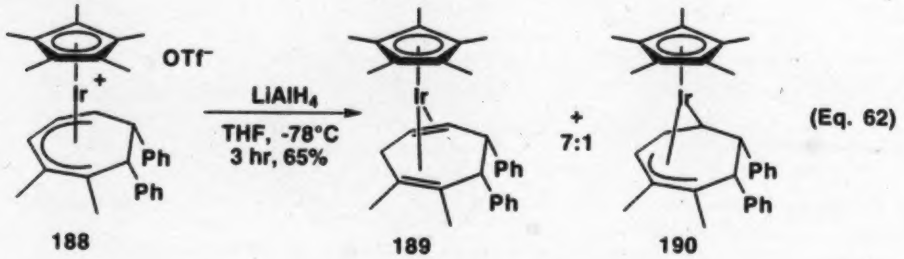
## I. Introduction and Background

Development of the cobalt-mediated [3 + 2 + 2] cycloaddition methodology for practical synthetic applications necessitates the removal of the organic fragment from the metal. Another desirable feature is the further selective functionalization of the cycloheptadienyl ring. Both of these requirements are met by the nucleophilic addition of a suitable anion to the coordinated cycloheptadienyl ligand, followed by a demetallation reaction to remove the functionalized organic fragment from the reduced metal center. In addition to activating an olefinic ligand towards nucleophilic addition, metals coordinated to an organic fragment also control the facial selectivity in a nucleophilic addition by blocking one face of the coordinated ligand. The chemistry of nucleophilic additions to transition metal complexes has been well studied and reviewed.[132]

Nucleophilic additions to $\eta^5$-cycloheptadienyl iron complexes have been extensively developed.[132b,c] A wide range of reactivity patterns has been observed, with the regioselectivity of the addition governed by the properties of the metal complex, ancillary ligands, and also the strength of the nucleophile itself. Several general trends in this iron reactivity manifold are notable. Soft nucleophiles add to the terminal position, following the DGM rules,[132a] while harder nucleophiles, such as alkyllithium reagents, selectively react at the C-2 position to produce $\eta^1$-$\eta^3$ $\sigma$-allyl cycloheptendiyl complexes. For our purposes, a soft nucleophile is desirable, as addition to the terminal position formally reduces the metal, rendering oxidative removal more feasible.

Nucleophilic additions to iridium cycloheptadienyl complexes shows different addition patterns.[62] Addition of $LiAlH_4$ to $Cp^*Ir(cycloheptadienyl)^+$ complex **188** in THF solution yields a 7:1 mixture of 1,4-cycloheptadiene complex **189** and the $\eta^1$-$\eta^3$-$\sigma$-

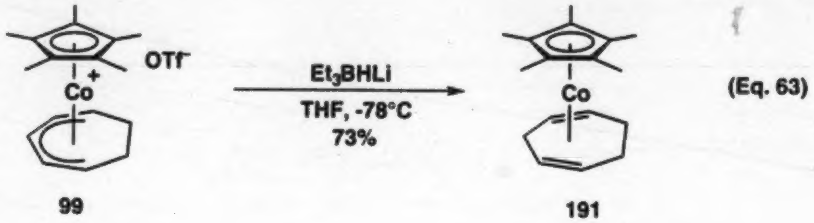
allyl complex **190** in a combined 65% yield (Eq. **62**).[62] The minor compound is a result of nucleophilic addition to the $C_2$ position, a pattern often seen in the addition of hard nucleophiles to iron cycloheptadienyl complexes.[132e] However, the major complex is a result of a less conventional addition to the central carbon of the cycloheptadienyl ring. The addition of $Et_3BHLi$ (Superhydride™) to [Cp*Ir(cycloheptadienyl)]$^+$ $Cl^-$ [125] in THF solution at -78°C yields exclusively Cp*Ir(1,4 cycloheptadiene), the product of central carbon addition.



(Eq. 62)

Several studies have been done on nucleophilic addition reactions to *cobalt* heptadienyl complexes as well. The reactions of ($\eta^5$-cyclopentadienyl)cobalt($\eta^5$-cycloheptadienyl)(III) cation **133** with nucleophilic phosphines give terminal addition products; this addition is reversible with the weakly nucleophilic triphenylphosphine.[112a,133] Hydride addition to this cation using $NaBH_4$ is reported to occur at the central position, as observed in iridium.[117a] More strongly basic carbanions[134] or organometallic anions[135] have been shown either to add to the central position or reduce the cation to a cobalt(II) radical species. This radical appears to thermodynamically unstable with respect to ligand coupling, as indicated by the observed ring dimerized product. Reductive dimerization of coordinated rings are not uncommon.[136] We have also noticed similar reductive reactivity in our attempts to add free radicals to the 18-electron cobalt cycloheptadienyl complexes (*vide infra*).

The addition of hard nucleophiles to cycloheptadienyl cobalt complex **99** occurs at the central position. The reaction of superhydride with complex **99** in THF solution, for example, produces the 1,4-cycloheptadiene complex **191** in good yield (Eq. **63**).[88]

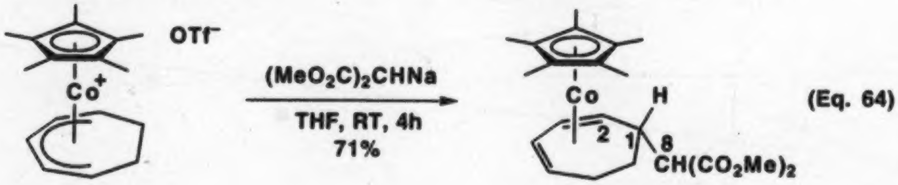


**99** **191**

## II. Results and Discussion

### A. *Nucleophilic Addition Reactions of Cycloheptadienyl Complexes*

The addition of a soft carbon nucleophiles to an ($\eta^5$-cycloheptadienyl)cobalt complex was expected to be regioselective for the terminal position of the $\eta^5$-pentadienyl framework, which generates a readily decomplexed diene complex. Sodium dimethylmalonate is a readily available, weakly nucleophilic anion prepared from dimethylmalonate and sodium hydride in THF solution. The reaction of this anion with the Cp*Co(cycloheptadienyl) cation **99** in THF solution at ambient temperature produces the terminal addition product **192** in good isolated yield (Eq. **64**). The

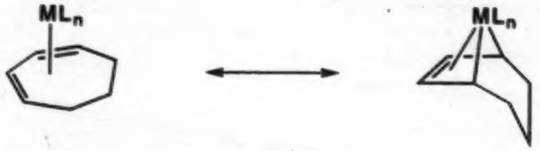


**99** **192**

conjugated $\eta^4$-cycloheptadiene structure and *exo*-stereochemistry are established by spectroscopic analysis, which indicates the formation of a non-symmetrical system. Further confirmation is obtained by spectroscopic comparison to analogous

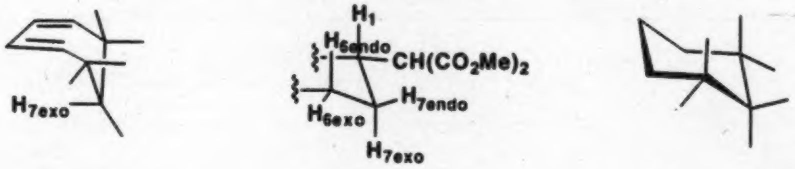
$(P(OPh)_3)Fe(CO)_2(\eta^4$-cycloheptadiene) systems as well as by full characterization.[99b] For convenience, the numbering system arbitrarily assigns the position of the malonate group to be the $C_1$ position. The $^1H$ NMR spectrum of cycloheptadiene complex **192** shows a characteristic set of signals for the malonate moiety. The methoxy groups appear as two singlets at $\delta$ 3.43 and $\delta$ 3.35, as expected for the diastereotopic esters. The malonyl CH signal at $\delta$ 3.34 is a highly characteristic doublet with a $J_{HH}$ value of 8.2 Hz to the adjacent $H_1$ atom on the ring. This provides a convenient handle for assigning the remaining signals from the ring hydrogen atoms. The COSY spectrum and standard homonuclear decoupling techniques allow the assignment of all the signals that are present in the $^1H$ NMR spectrum. The allylic $H_1$ signal resonates at $\delta$ 2.49 and has a surprisingly small value (1.7 Hz) for the $J_{1\text{-}2}$ coupling constant, indicating a dihedral angle of nearly 90° between $H_1$ and $H_2$. The chemical shift of the $H_2$ olefinic hydrogen atom, 2.21 ppm, indicates a significant amount of back donation from the diene to the metal and apparent rehybridization of this carbon toward $sp^3$ character (Figure **10**), a common feature of electron rich metal $\eta^4$-diene complexes.[137] In contrast, the internal protons of the diene resonate at $\delta$ 4.07 ($H_3$) and $\delta$ 4.01 ($H_3$), respectively.

**Figure 10**. Cycloheptadiene Complex Resonance Structure.



These two signals apparently reflect less rehybridization of the internal carbons of the diene relative to the terminal positions, in agreement with the proposed structure depicted in Figure **10**. The remaining terminal diene proton ($H_5$) resonates upfield at 2.16 ppm. As can be seen in Table **5**, most coupling constants along the diene portion of the molecule are somewhat smaller (5-7 Hz) than the expected *cis* coupling constant for an alkene (ca 10 Hz).[97] This presumably reflects the donation of electron density from the metal and slight rehybridization. Similar to the $J_{1\text{-}2}$ coupling constant (where $H_1$ is *endo* to the metal), $J_{5\text{-}6endo}$ is rather small (1.6 Hz), although $J_{5\text{-}6exo}$ is 6.5 Hz. The resonance assigned to $H_{6exo}$ appears at δ 1.65 as a complex multiplet. Its geminal partner, $H_{6endo}$, is a resolved dddd pattern with two large coupling constants, $J_{6endo\text{-}6exo}$ and $J_{6endo\text{-}7exo}$, both of which have values of around 13 Hz. The remaining signals resonate at 1.34 ppm ($H_{7endo}$) and 0.84 ppm ($H_{7exo}$). Although the $H_{7endo}$ signal is quite broad and unresolved due to several small coupling constants, the $H_{7exo}$ signal has a well-resolved "qd" multiplicity pattern, in which three coupling constants ($J_{7exo\text{-}7endo}$, $J_{7exo\text{-}1}$ and $J_{7exo\text{-}6endo}$) are all approximately 12 Hz, resulting in an apparent quartet. The remaining small coupling constant of 3.8 Hz attributed to $J_{7exo\text{-}6exo}$. This is expected for the conformation depicted in Figure **11**, where both geminal and "anti"-like coupling constants are large. This signal is normally quite well resolved and far enough upfield to be considered as a characteristic signal in the $^1$H NMR spectra of cycloheptadiene complexes in general. This structural feature is analogous geometrically to the chair conformation of cyclohexane rings (Figure **11**) and serves to define the stereochemistry of the malonate substituent as *exo*, as anticipated.

**Figure 11.** Geometry of Cycloheptadiene Complexes



Pearson has also noted a strong upfield shift in one methylene hydrogen in related $(PR_3)Fe(CO)_2(\eta^4\text{-cycloheptadiene})$ systems.[99] This shift can be readily explained if the proton is situated more or less directly under the π-system. The $7_{exo}$ proton is apparently significantly shielded by the diene fragment resulting in a relatively far upfield shift. This observation has also been made in several other organometallic complexes.[100]

**Table 5**. Comparative $^1$H NMR Spectroscopic Data for Malonylcycloheptadiene Complexes

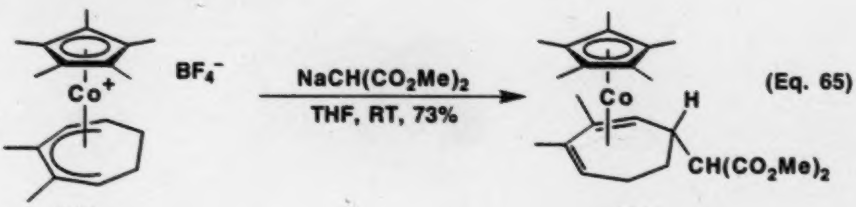
| | **192** | **195** | **196** | **197** | **201** | **199** |
|---|---|---|---|---|---|---|
| **H$_1$**<br>$J_{1\text{-}2}$ | 2.49(dddd)<br>1.7 Hz | 2.59(dddd)<br>1.6 Hz | 2.53(m)<br><2 Hz | 2.71 ("t")<br>small | 2.58(dddd)<br>1.3 Hz | 3.15 (m)<br>7.5 Hz |
| **H$_2$**<br>$J_{2\text{-}3}$ | 2.21 (br d)<br>6.8 Hz | 2.15 (m)<br>7.0 Hz | 1.96 (d)<br>7.2 Hz | 2.66 (s)<br>b | 2.18 (d)<br>7.3 Hz | 2.58 (t)<br>7.5 Hz |
| **H$_3$**<br>$J_{3\text{-}4}$ | 4.07 (dd)<br>4.5 Hz | 3.98 (dd)<br>4.7 Hz | 3.80 (dd)<br>4.9 Hz | b | 3.58 (dd)<br>4.9 Hz | 3.86 (dd)<br>4.5 Hz |
| **H$_4$**<br>$J_{4\text{-}5}$ | 4.01 (dd)<br>6.9 Hz | 3.85 (dd)<br>7.0 Hz | 4.12 (d)<br>b | 5.93 (s)<br>b | 4.18 (d)<br>b | 4.54 (d)<br>b |
| **H$_5$**<br>$J_{5\text{-6endo}}$<br>$J_{5\text{-6exo}}$ | 2.16 (br t)<br>1.6 Hz<br>6.5 Hz | 2.15 (m)<br>b<br>a | b | b | b | b |
| **H$_{6\text{endo}}$**<br>$J_{6\text{endo-6exo}}$<br>$J_{6\text{endo-7endo}}$<br>$J_{6\text{endo-7exo}}$ | 1.48(dddd)<br>13 Hz<br>3.5 Hz<br>12.8 Hz | b | b | 1.85 (ddd)<br>16 Hz<br>3.0 Hz<br>12.4 Hz | b | b |
| **H$_{6\text{exo}}$**<br>$J_{6\text{exo-7endo}}$<br>$J_{6\text{exo-7exo}}$ | 1.65 (m)<br>a<br>3.8 Hz | 1.65 (m)<br>a<br>a | 1.15 (m)<br>3.4 Hz<br>3.8 Hz | 1.70 (ddd)<br>3.4 Hz<br>2.9 Hz | 0.95[c]<br>a<br>a | 0.66 (m)<br>a<br>4.2 Hz |
| **H$_{7\text{endo}}$**<br>$J_{7\text{endo-7exo}}$<br>$J_{7\text{endo-1}}$ | 1.34 (br d)<br>12.7 Hz<br>3.5 Hz | 0.95 (m)<br>a<br>3.7 Hz | 0.90 (m)<br>12.3 Hz<br>3.4 Hz | 1.55 (d)<br>16 Hz<br>small | 1.8[c]<br>a<br>3.6 Hz | 1.55[a]<br>12 Hz<br>a |
| **H$_{7\text{exo}}$**<br>$J_{7\text{exo-1}}$ | 0.84 (qd)<br>11.9 Hz | 0.95 (m)<br>11.4 Hz | 0.80 (dt)<br>12.3 Hz | 0.67 (qd)<br>12.4 Hz | 1.8[c]<br>11.6 Hz | 1.16 (ddd)<br>12 Hz |
| **H$_8$**<br>$J_{8\text{-}1}$ | 3.34 (d)<br>8.2 Hz | 3.21 (d)<br>8.3 Hz | 3.18 (d)<br>8.3 Hz | 3.60 (d)<br>9.9 Hz | 3.30 (d)<br>8.5 Hz | 3.09 (d)<br>11.4 Hz |

[a] Numerical value of the coupling constant could not be determined due to overlapping signals. [b] Not applicable. [c] Resonances are not resolved in the $^1$H NMR spectrum. Chemical shift is estimated from the COSY spectrum.

The apparent rehybridization of the diene suggested by the $^1$H NMR spectrum is supported by the $^{13}$C NMR spectrum. Although the carbon signals for the internal positions of the diene are shifted upfield to 82.1 ppm ($C_4$) and 80.0 ppm ($C_3$), the respective values for the $^1J_{CH}$ coupling constants are 162 and 159 Hz, which are relatively unchanged from sp$^2$ hybridization. The terminal positions of the diene show more perturbation; carbons two and four are identified by heteronuclear correlated spectroscopy as the signals at 52.6 ppm ($^1J_{CH}$ = 145 Hz) and 53.0 ppm ($^1J_{CH}$ = 146 Hz). These reduced values suggest that some rehybridization has in fact occurred. The remaining carbon signals, for $C_1$, $C_6$ and $C_7$, resonate at 39.8, 28.9 and 27.9 ppm, respectively, and have $^1J_{CH}$ values of 125-135 Hz, which are typical of sp$^3$ hybridized carbon atoms.

Some degree of back donation is evident in all of the cobalt (I) cycloheptadiene complexes prepared by alkylation: **195-197**, **199** and **201** (Table **5**). The diene hydrogen atoms are all shifted upfield from the normal olefinic (δ 5-7) range. The central ($H_3$ and $H_4$) positions are only slightly shifted upfield to about 4 ppm. In contrast, the protons on the terminal carbon atoms of the diene are dramatically shifted to slightly under 2 ppm. $^{13}$C NMR data also show substantial perturbation from a normal diene. The chemical shifts of the terminal positions are usually 50-60 ppm; in contrast, the internal positions resonate at 80-90 ppm. The different hybridization determined from the $^1J_{CH}$ coupling constants is also general. The internal olefin carbons consistently have a $J$ value of close to 160 Hz, indicating substantial sp$^2$ character. The terminal positions exhibit a coupling constant of about 140-155 Hz, somewhat re-hybridized towards sp$^3$.

The solid state conformation of the cobalt cycloheptadiene complexes has been confirmed by the X-ray crystal structure of complex **194**, prepared from the addition of sodium dimethylmalonate in THF to dimethylcycloheptadienyl complex **193** (Eq. **65**). The cycloheptadienyl complex **193** is not prepared from the normal [3 + 2 + 2] allyl/alkyne cycloaddition reaction and its preparation and characterization will be discussed in a later chapter. The malonate anion adds exclusively to the less hindered terminus of the pentadienyl framework ($C_5$); even a single methyl group one position removed from the terminus is apparently enough to hinder the approach of the nucleophile from the opposite side.

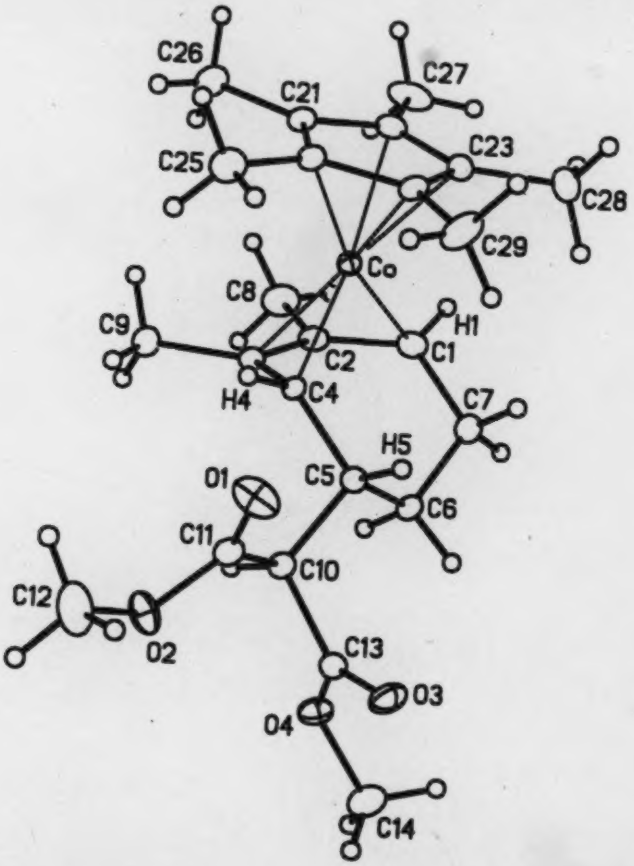


**193** **194** (Eq. 65)

The $^1H$ NMR spectrum of **194** is fully consistent with the spectra of other malonate adducts. The two diene hydrogen atoms ($H_2$ and $H_5$) resonate at $\delta$ 2.00 as a single multiplet. The most downfield signal of the ring, $H_1$, resonates at $\delta$ 2.31, and shares a 7.4 Hz coupling constant with the malonate methine at 3.32 ppm. The most upfield signal, $H_{7exo}$, is a quartet of doublets, exhibiting a large quartet-like multiplicity pattern of about 12 Hz and a smaller doublet of 3.5 Hz. The remaining hydrogen atoms, $H_{6endo}$ and $H_{7endo}$, resonate at $\delta$ 1.70 and $\delta$ 1.28, respectively. The $^{13}C$ NMR spectrum also indicates a disubstituted diene structure; two quaternary carbons attributed to $C_3$ and $C_4$ are found at 88.7 and 87.3 ppm. The terminal carbon atoms of the diene resonate at 53.7 and 53.6, and have $^1J_{CH}$ values of 141 Hz.

The malonate adduct **194** crystallizes from a concentrated pentane solution at -35°C to form light orange crystals. An X-ray diffraction analysis (Figure **12**) carried out on complex **194** confirms both the *exo* malonate substituent and the position of the $7_{exo}$ hydrogen atom underneath the diene moiety. The three saturated carbon atoms of the cycloheptadiene ring are in the highly structured geometry proposed in Figure **11**, strongly resembling the chair conformation of a cyclohexane ring.

**Figure 12.** ORTEP[115] for Complex **194** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS9609



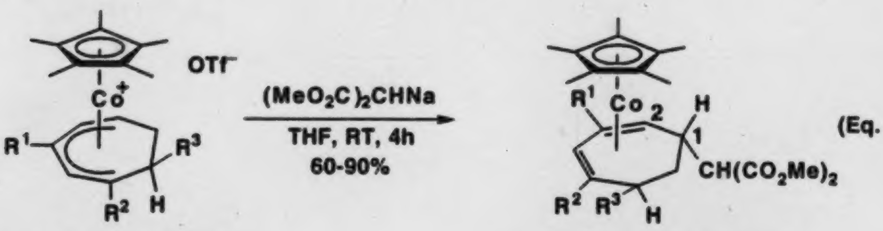
Final Residuals: $R_1 = 0.0547$; $wR_2 = 0.1341$. Data obtained at -60°C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): Co-C1, 1.984(4); Co-C2, 1.987(4); Co-C3, 1.977(4); Co-C4, 2.009(4); C1-C2, 1.443(6); C1-C7, 1.508(6); C2-C3, 1.422(6); C2-C8, 1.504(6); C3-C4, 1.444(6); C3-C9, 1.511(6); C4-C5, 1.504(6); C5-C6, 1.527(6); C5-C10, 1.542(6); C6-C7, 1.504(6); C10-C11, 1.516(6); C10-C13, 1.514(6).

Selected Bond Angles (deg.): C2-C1-C7, 128.4(4); C1-C2-C3, 116.4(4); C1-C2-C8, 120.7(4); C3-C2-C8, 122.2(4); C2-C3-C4, 117.0(4); C2-C3-C9, 122.7(4); C4-C3-C9, 119.9(4); C3-C4-C5, 126.5(4); C4-C5-C6, 113.5(4); C4-C5-C10, 107.8(3); C6-C5-C10, 109.3(3); C5-C6-C7, 113.2(4); C1-C7-C6, 114.0(4); C5-C10-C11, 112.7(4); C5-C10-C13, 112.4(3); C11-C10-C13, 107.5(3).

Certain other structural features are slightly unusual. The four carbons of the diene are virtually coplanar, as expected; the torsional angle is only 2°. However, the bond lengths are nearly identical. Diene fragments coordinated to electron-rich metal centers are expected to have a long-short-long carbon-carbon bond length pattern.[2] In this complex, the $C_1$-$C_2$ and $C_4$-$C_3$ bond lengths are practically identical (1.443(6) and 1.444(6) Å), while the $C_2$-$C_3$ bond length, expected to be significantly shorter, is only marginally different (1.422(6) Å). All these bond lengths are significantly lengthened from the normal C=C bond length of about 1.34 Å, indicating significant rehybridization. The methyl groups are slightly bent up toward the cobalt center by about 7-9°.

The reactions between sodium dimethylmalonate and the substituted cycloheptadienyl complexes establish a fair degree of generality to the nucleophilic addition reaction. Methyl, dimethyl, and diphenyl complexes **101**, **102** and **95** all undergo reaction with malonate anion to yield products of terminal attack (Eq. **66**). All compounds are obtained as red, mildly air sensitive oils, with the exception of the parent malonate adduct **192**, which slowly solidifies when pure. In all of these complexes, the malonate provides a convenient spectroscopic handle for the assignment of individual signals. The ring position occupied by the malonate is easily discerned by homonuclear decoupling or 2D NMR spectroscopic techniques. Other spectroscopic similarities are also evident (Table **5**).

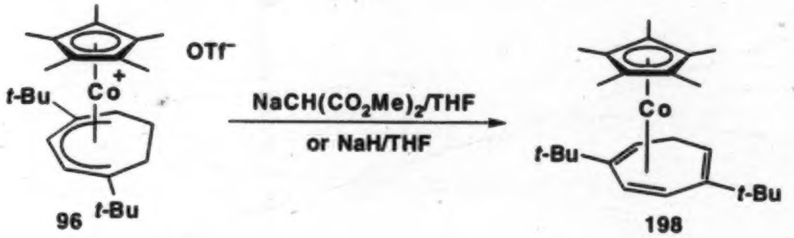


(Eq. 66)

**101** $R^1$, $R^2$ = H, $R^3$ = Me
**102** $R^1$ = H, $R^2$, $R^3$ = Me
**95** $R^1$, $R^2$ = Ph, $R^3$ = H

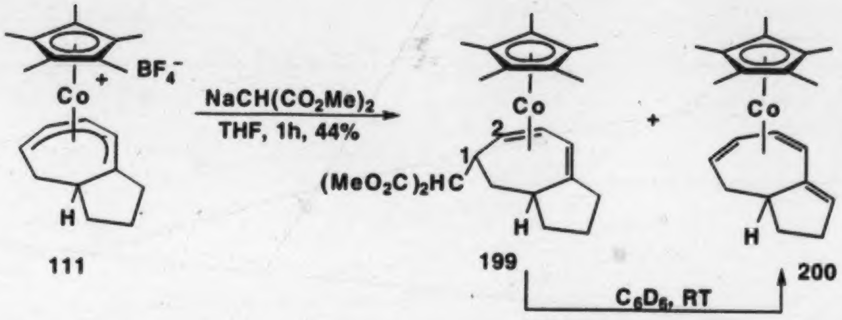
**195** $R^1$, $R^2$ = H, $R^3$ = Me
**196** $R^1$ = H, $R^2$, $R^3$ = Me
**197** $R^1$, $R^2$ = Ph, $R^3$ = H

However, in some cycloheptadienyl complexes, the steric profile changes the reaction pathway. The di-*t*-butyl complex **96** undergoes deprotonation in the ring to form a 1,4 di-*t*-butyl-1,3,5-cycloheptatriene complex **198**, tentatively assigned by $^1$H NMR spectroscopy (Eq. **67**). Apparently the adjacent *t*-butyl group is too large to allow approach of the nucleophile to the preferred terminal position. Interestingly, deprotonation appears to occur at the *t*-butyl substituted end of the pentadienyl fragment, generating a symmetric ring system. The $\eta^4$-coordination to the cobalt center disrupts this symmetry and each individual proton is observed. The high acidity of the *exo* ring proton is due to the role of the cobalt cation as a highly effective "leaving group", as in an $E_2$ reaction. Complex **198** has previously been synthesized by allowing cycloheptadienyl complex **96** to react with stronger bases, such as NaH.[88]



(Eq. 67)

There are other factors aside from the steric profile to consider. Nucleophilic addition of malonate anion to the bicyclic cycloheptadienyl complex **111** provides a mixture of addition (**199**) and deprotonation (**200**) products (Eq. **68**). Furthermore, addition appears to be reversible, as the sample slowly converts predominantly to the deprotonation product **199**. The triene structure is assigned as shown based on the triplet at δ 5.65, which does not show any coupling to the other four hydrogen atoms assigned to the coordinated diene. The cycloheptatriene isomer would be expected to show coupling all along the unsaturated framework. No attempt was made to determine whether the reaction can be driven to completion, exclusively forming the triene complex.

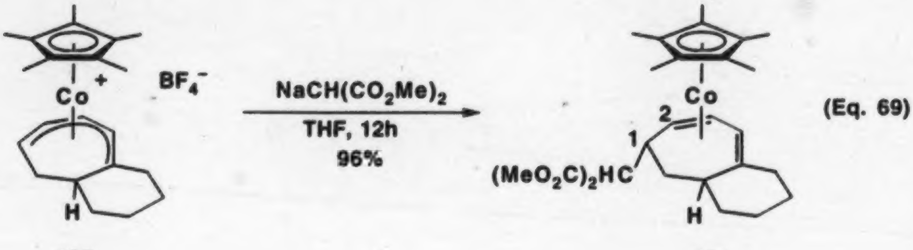


(Eq. 68)

The malonyl cycloheptadiene **199** can be prepared selectively by utilization of short reaction times and storage at low temperature to slow the ensuing rearrangement. The bicyclic malonate adduct is obtained in moderate yield (44%) using a shorter reaction time, yet some deprotonation product is still observed in the $^1$H NMR spectrum. Other studies on the reactivity of cobalt cycloheptadienyl complexes suggest that the deprotonation product may be obtained cleanly and directly by treatment with a strong base.$^{88}$

The bicyclo[5.3.0] ring system of complex **199** is spectroscopically as well as chemically slightly different from the other malonate adducts. Although the overall features are similar (Table **5**), some of the observed coupling constant values are substantially different from those obtained for related complexes. This indicates a slightly altered coordination geometry or, more likely, a change in the ground state conformation of the seven-membered ring. It is reasonable that the five-membered ring places different conformational constraints on the saturated portion of the other ring, resulting in an altered structure. This distorted conformation is indicated by the much larger $J_{1\text{-}2}$ value of 7.5 Hz for this system. In all other malonate adducts, this value is very small, averaging 1.3-1.7 Hz (Table **5**). Other values apparently differ as well, but as the compound could not be obtained free of triene impurities, rigorous assignment of all the coupling constant values was not possible.

In contrast to the bicyclo[5.3.0]decadienyl system **111**, the reaction of the bicyclo[5.4.0]undecadienyl complex **105** with malonate cleanly generates the malonate adduct **201**. Cycloheptadienyl complex **105** is assumed to have the same *endo* stereochemistry as **111** at the ring junction, thus the malonate adduct is assigned the stereochemistry shown in Eq. **69**. The diene complex **201** is isolated in high yield (96%) as a deep red air sensitive oil.



**105** **201**

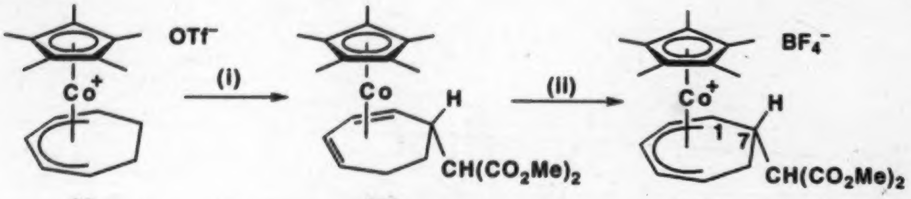
The lack of clean addition of malonate to cycloheptadienyl complex **111** cannot be explained by steric arguments since the opposite end of the pentadienyl framework is unhindered. A difference in the acidity of the H atom of the methylene or a subtle change in conformational ground state energy must be responsible for the change in reactivity. It is unclear why the [5.4.0] system **105** should have a lower kinetic acidity than that of the [5.3.0] system **111**. Although complex **201** potentially can be thermolytically converted to a triene complex analogous to **200** or formed by the reaction of **105** with a strong non-nucleophilic base, no attempt was made to determine the feasibility of these reactions.

### *B. Sequential Functionalization of Cycloheptadienyl Complexes*

As previously discussed, transition metals can control the facial selectivity of reactions by blocking one side of the coordinated ligand. This is a desirable feature for organic synthesis, as it allows for consecutive ring functionalization to be made in a fully stereocontrolled manner. Pearson[99] has previously shown that consecutive additions can be conducted on a closely related cycloheptadienyl iron system, resulting in the formation of *cis*-1,3-disubstituted seven-membered rings.

The cobalt system is also amenable to such sequential addition chemistry. A simple procedure to convert the cycloheptadienyl complex **99** to the malonyl-cycloheptadienyl complex **202** is illustrated in Scheme **36**. Addition of malonate anion to form **192** is followed by hydride abstraction by triphenylmethyl cation to produce complex **202** in good overall yield (52%) as a light orange, air stable powder after purification by flash chromatography. Complex **202** has a $^1$H NMR spectrum

**Scheme 36**



**99** **192** **202**

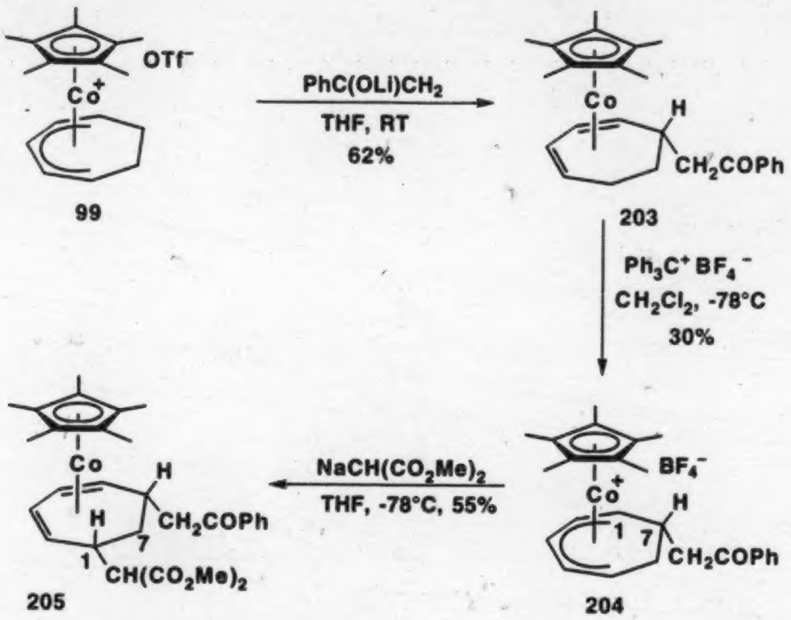
i) $(MeO_2C)_2CHNa$, THF, RT, 87%
ii) $Ph_3C^+$ $BF_4^-$, $CH_2Cl_2$, -78°C, 60%

characteristic of cycloheptadienyl complexes (see Table **2**, page 59), with 5 downfield signals at 6.71 ($H_3$), 5.47 ($H_4$), 4.89 ($H_2$), 4.40 ($H_1$) and 4.23 ($H_5$) ppm, all consistent with the observed pattern for cycloheptadienyl complexes. The $H_5$ signal is correlated to a geminal pair at 1.88 ($H_{6exo}$) and 0.14 ($H_{6exo}$) ppm, which share a 12 Hz coupling constant. A multiplet at 3.62 ppm is attributed to $H_{7endo}$ based on correlations in the COSY spectrum to $H_1$, $H_{6exo}$, $H_{6endo}$ and the malonate CH ($H_8$). Also present in the spectrum are two singlets at δ 3.72 and 3.67, attributed to the diastereotopic methyl ester groups of the malonate. The $^{13}$C NMR spectrum is also characteristic of cycloheptadienyl complexes, with five downfield sp$^2$ carbon signals resonating at 101.2 ($C_3$), 99.8 ($C_4$), 97.6 ($C_2$), 89.6 ($C_5$) and 84.7 ($C_1$) ppm, with $^1J_{CH}$ values of 167-176 Hz for $C_{2-4}$ and 159 Hz and 150 for $C_1$ and $C_5$, respectively. The malonate shows signals at δ 169.7 and 53.0 for the ester group and $C_8$ resonates at 56.2 ppm. Unlike the corresponding diene complex, only one signal is observed for both ester carbonyl groups, indicating less of a difference in the diastereotopic space experienced by the two ester groups.

Further addition of nucleophiles to the cation **202**, however, is complicated by competitive side reactions, giving an uncharacterized mixture of products. The malonate group is highly acidic; it may be that deprotonation of the acidic malonate hydrogen or the cycloheptadienyl ring occurs first. Subsequent intramolecular reactions ensue that generate a number of different products.

The use of a nucleophile that is less acidic than malonate proves more amenable to sequential nucleophilic additions. The reaction of the lithium enolate of acetophenone with the cycloheptadienyl complex **99** produces the cobalt diene complex **203**, tentatively identified by its $^1$H NMR spectrum and used without further characterization (Scheme **37**). Complex **203** is converted to the cationic cycloheptadienyl complex **204** by hydride abstraction with trityl tetrafluoroborate in a modest, non-optimized yield. The pentadienyl fragment of **204** is identified by a triplet at δ 6.69, assigned to $H_3$, as well as four other downfield signals attributed to the cycloheptadienyl ring. Three sets of resonances in the range 7.86-7.43 are indicative of the phenyl group. The characteristic upfield signal for $H_{6exo}$ is seen at δ 0.04. The ring substituent of **204** is attached to $C_7$, similar to complex **202**, as shown by the HMQC spectrum, which also shows that $H_{6exo}$ (0.04 ppm) and $H_{6endo}$ (2.05 ppm) are attached to the same carbon atom ($C_6$, 31.5 ppm). The $C_7$ signal resonates at 49.3 ppm and shows one bond correlations ($^1J_{CH}$) to only one hydrogen, $H_{7endo}$ (3.60 ppm). In the COSY spectrum, this proton signal is seen to be correlated to 4.54 ($H_1$), 2.05 ppm ($H_{6endo}$) and 0.04 ppm ($H_{6exo}$). A set of correlations is also seen between $H_7$ and two signals at 2.93 and 2.77 ppm, which are thus assigned to the diastereotopic methylene AB unit of the substituent. The carbonyl carbon of the substituent resonates at δ 197.9 in the $^{13}$C NMR spectrum, as expected for acetophenone. A single IR stretching frequency for the carbonyl is observed at 1680 cm$^{-1}$.

Scheme 37


OTf⁻
Co
PhC(OLi)CH₂
THF, RT
62%
Co
H
CH₂COPh
99
203
Ph₃C⁺ BF₄⁻
CH₂Cl₂, -78°C
30%
Co
H
H
CH₂COPh
7
1
CH(CO₂Me)₂
NaCH(CO₂Me)₂
THF, -78°C, 55%
BF₄⁻
Co
H
1
7
CH₂COPh
205
204

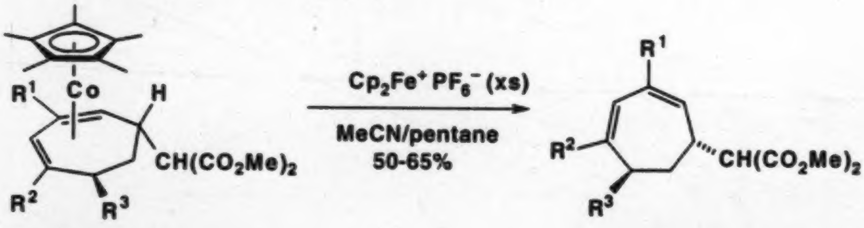
Subsequent addition of the weaker malonate anion to the substituted $\eta^5$-cycloheptadienyl complex **204** provides a product identified as the 1,3 disubstituted cycloheptadiene **205**. As a diene complex, oxidative removal of the organic ring system from the cobalt template should be facile (*vide infra*), although this was not attempted. Cycloheptadiene complex **205**, numbered according to the rule that the malonate substituent defines the $C_1$ atom of the cycloheptadienyl ring, is readily identified by its $^1H$ NMR spectrum which contains both phenyl resonances at $\delta$ 7.82-7.00 and methyl signals at $\delta$ 3.38 and 3.34. The malonate CH group ($H_8$) resonates at $\delta$ 3.29 (d, $J = 7.5$ Hz), coupled to the ring proton at $\delta$ 2.54 ($H_1$). The $CH_2$ of the acetophenone group ($H_{9a}$ and $H_{9b}$) are diastereotopic and the individual hydrogen atoms resonate at $\delta$ 2.65 and 2.42. Interestingly, the coupling constants observed from the $CH_2$ group to the ring hydrogen at $\delta$ 2.36 ($H_6$) are different for each diastereotopic methylene hydrogen: 8.4 and 5.1 Hz, respectively. The remaining proton signals are readily assigned using the two starting points described above. The diene section closely resembles less substituted cobalt cycloheptadiene complexes (Table **5**): the inner hydrogen atoms resonate further downfield at $\delta$ 4.04 ($H_3$) and $\delta$ 3.93 ($H_4$) and the terminal hydrogens are located upfield at $\delta$ 2.26 ($H_2$) and $\delta$ 2.18 ($H_5$). Although the $H_{7endo}$ signal is a relatively unremarkable multiplet centered at $\delta$ 2.35, the $H_{7exo}$ signal is a clean apparent quartet with an observed coupling constant of 12 Hz, consistent with the expected chair-like geometry of the $sp^3$-hybridized portion of the ring. In the $^{13}C$ NMR spectrum, three carbonyl signals are seen at $\delta$ 198.4 (C(O)Ph), 169.0 and 168.7 (ester groups). The diene carbons are located at 80.7 ($C_4$), 80.6 ($C_3$), 57.2 ($C_5$), and 53.1 ($C_2$) ppm, with $^1J_{CH}$ values of 164-165 ($C_{3/4}$) and 144-146 ($C_{2/5}$), similar to the patterns observed in other cycloheptadiene cobalt complexes (*vide supra*). The remaining two carbons of the ring resonate at 35.9 ($C_6$) and 34.3 ppm ($C_7$). The carbons directly attached to the ring ($C_8$ and $C_9$), from the malonate and acetophenone groups, resonate at 60.1 and 48.8 ppm, respectively. There are several carbonyl bands observed in the infra-red spectrum at 1745, 1735, 1717 and 1681 $cm^{-1}$. The low wavenumber signal arises from the ketone group, while the other signals come from the ester groups as well as a tentatively assigned Fermi resonance, arising from an interaction with the overtone of a signal at 868 $cm^{-1}$. Other cobalt cycloheptadiene complexes with the malonate unit show IR bands at around 1755 and 1735 $cm^{-1}$.

### *C. Oxidative Removal of the Coordinated Cycloheptadiene*

There are several established methods for decomplexing coordinated dienes from cobalt(I) complexes. Oxidative removal, displacement by ligand exchange reactions, and base-induced ligand aromatization (for six-membered ring systems) are all commonly used methods.[138] However, for our system, the oxidative removal appears to be the most reasonable option. Cobalt(I) conjugated diene complexes are not generally very labile; thus, displacement reactions are likely to require forcing conditions that are conducive to isomerization of the free diene. Oxidative removal, in contrast, has a greater chance of returning the diene unchanged. Cobalt(II) complexes are substitutionally labile, while cobalt(III) complexes are electron poor and unable to strongly coordinate dienes through $\pi$-back donation. Potentially, a complex in either the cobalt(II) or cobalt(III) oxidation state would readily release the coordinated ligand.

Several oxidants are routinely used in the oxidative decomplexation of coordinated dienes to late metals. When assayed, standard oxidants[138] such as $Ce(NH_4)_2(NO_3)_6$, $Pb(OAc)_4$, $FeCl_3$/ethanol, $CuCl_2$ and other, stronger, oxidants fail to yield tractable organic material from the reaction with cobalt complex **192**. It was found, however, that treatment with ferricenium hexafluorophosphate yields small amounts of cycloheptadiene **206** upon reaction with the coordinated diene complex **192**. Further development of decomplexation with this oxidant led to partially optimized reaction conditions involving a two-phase solvent system of pentane and acetonitrile. This solvent system has previously been used in reactions with stronger oxidants such as $Ce(NH_4)_2(NO_3)_6$.[138c,i]

Decomplexation of the cycloheptadiene complexes **192** and **195-197** is carried out by the slow addition of a pentane solution of the diene complex to a cold, rapidly stirring solution of excess oxidant in acetonitrile (Eq. **70**). In this way, organic cycloheptadienes **206** to **209** are obtained in 50-65% yield as colorless to slightly yellow oils after workup and purification by flash chromatography.



(Eq. 70)

**192** R$^1$, R$^2$, R$^3$ = H
**195** R$^1$, R$^2$, R$^3$ = H, H, Me
**196** R$^1$, R$^2$, R$^3$ = H, Me, Me
**197** R$^1$, R$^2$, R$^3$ = Ph, Ph, H

**206** R$^1$, R$^2$, R$^3$ = H
**207** R$^1$, R$^2$, R$^3$ = H, H, Me
**208** R$^1$, R$^2$, R$^3$ = H, Me, Me
**209** R$^1$, R$^2$, R$^3$ = Ph, Ph, H

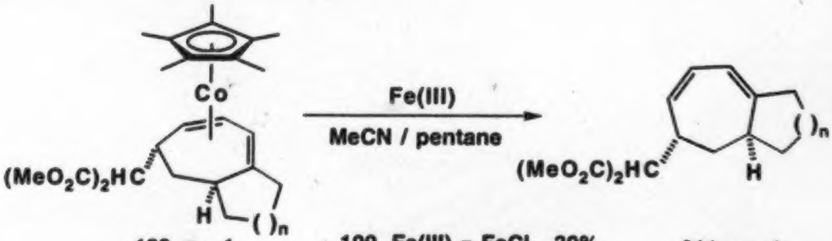
Pearson has also synthesized several related cycloheptadiene compounds and reports low field $^1$H NMR data for the unsubstituted compound **206**.[99] Although the data obtained for diene **206** agree with Pearson's report, the $^1$H NMR spectrum for **207** appears to be quite different from Pearson's *cis*-dimethyl-(6-methylcyclohepta-2,4-dien-1-yl)malonate. Compound **207** is therefore assigned as the *trans*-isomer. This result is consistent with the *endo*-stereochemistry observed in the X-ray crystal structure of bicyclo[5.3.0]decandienyl complex **111** and the expected *exo* alkylation using malonate anion. Pearson reports a single multiplet that integrates to four protons at 1.77-1.60 ppm in the 60 MHz $^1$H NMR spectrum, assigned to the hydrogen atoms attached to the sp$^3$ carbon centers. The observed spectrum for **207** shows three distinct multiplets centered at 3.05 ($H_1$), 2.50 ($H_6$) and 1.7 ppm (2H, $H_7$), assigned to the saturated methylene groups in the molecule. A signal at $\delta$ 5.7 (m, $H_{2-5}$) is assigned to the diene hydrogen atoms in the molecule. The methine hydrogen of the malonate resonates at $\delta$ 3.51 (d, $J = 9.0$ Hz) and the esters of the malonate substituent resonate at $\delta$ 3.72 and $\delta$ 3.71. The $^{13}$C NMR spectrum is also consistent with the proposed structure; four sp$^2$-hybridized methine signals are observed at $\delta$ 140.1, 133.8, 125.7 and 122.9, with $^1J_{CH}$ values between 145 and 161 Hz. A carbon signal resonating at 37.2 ppm ($C_1$ and $C_7$) is shown by the HMQC spectrum to correlate to both $H_1$ and $H_7$. The remaining ring carbon, $C_6$, resonates at $\delta$ 33.4. The malonate substituent is represented by carbon signals at $\delta$ 168.8 (carbonyl), 56.1 (methine), and 52.4 (methyl). In the IR spectrum, two carbonyl stretching frequencies are seen at 1756 and 1737 cm$^{-1}$.

In addition to the cycloheptadiene compound, two other products of the oxidation are obtained. Ferrocene is produced by the reduction of the ferricenium oxidant and the known[139] dicationic cobalt complex $Cp^*Co(NCMe)_3^{++}$ $(PF_6^-)_2$ can be recovered in good yield from the acetonitrile layer after extraction of the organic product into pentane. Although this overall procedure is not catalytic, this process demonstrates the potential to recycle the Cp*Co fragment.

We hypothesize that the initial oxidation to cobalt(II) is facile, but that this oxidation state is highly reactive, and in the absence of excess oxidant and/or a suitable ligand, extensive decomposition of the cycloheptadiene occurs. In the two phase system, the pentane layer contains the bulk of the cobalt diene and the organic diene. The organic diene is thus protected from the effects of excess oxidant. The cobalt diene complex is only slightly soluble in acetonitrile, so that in this phase there is always an excess of oxidant. This minimizes the time required for the second oxidation to occur, lessening decomposition, and provides a large excess of a suitable ligand: acetonitrile. The remaining cobalt fragment is therefore stabilized, which prevents further interaction with the organic product.

The bicyclic malonate adduct **201** is also easily demetallated in good (62%) yield by treatment with ferricenium under the above conditions to give *cis*-bicyclo[5.4.0]undecadiene **210** (Eq. **71**). This bicyclic diene shows several features in the $^1$H NMR spectrum that clearly show the diene structure, notably the two multiplets centered at $\delta$ 5.67 (2H) and 5.58 (1H). A malonate methine at $\delta$ 3.55, and two methyl esters that resonate at $\delta$ 3.74 and $\delta$ 3.72 are also quite characteristic. The remainder of this spectrum consists of a series of poorly resolved multiplets. The $^{13}$C NMR spectrum is also consistent with a trisubstituted diene fragment. The unsaturated carbon of the ring fusion, an sp$^2$-hybridized quaternary carbon, resonates at $\delta$ 149.8. The three other carbons of the diene fragment are located at 132.7, 125.7, and 118.4, with $^1J_{CH}$ values of 160, 155, and 148 Hz, respectively. Two IR bands at 1756 and 1737 cm$^{-1}$ are attributed to the malonate carbonyl groups.

The use of ferric chloride as the oxidant in the [5.3.0] system **199** gives a lower yield (39%) of diene **211**, although it is uncertain if this is due to the change in oxidant or to the system itself. Three well-resolved signals are observed in the $^1$H NMR spectrum at $\delta$ 5.81, 5.68, and 5.60, attributed to $H_3$, $H_4$, and $H_2$, respectively. Again, many of the remaining signals are complex overlapping multiplets, but the malonate methine hydrogen is clearly visible at δ 3.41 (d, $J$ = 10.5 Hz), and a separate multiplet at 3.22-3.13 ppm is readily assigned to the $H_1$ hydrogen atom based on the COSY spectrum. Several signals in the $^{13}C$ NMR spectrum at δ 154.4, 129.4, 126.6 and 116.0, are readily attributed to the diene group. Two carbonyl bands at 1750 and 1736 $cm^{-1}$ are again observed in the infrared spectrum. The bicyclic [5.4.0] and [5.3.0] ring systems form the core of several important classes of natural products and this route provides an unusually facile synthesis of these valuable molecules.[140]



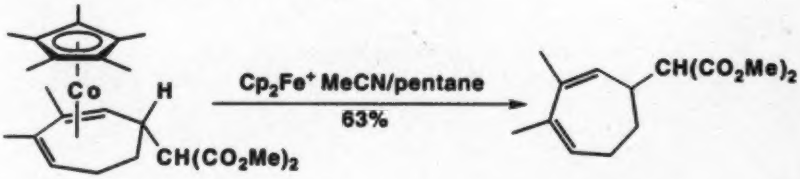
(Eq. 71)

**199**, n = 1
**201**, n = 2

**199**, Fe(III) = $FeCl_3$, 39%
**201**, Fe(III) = $Cp_2Fe^+$, 62%

**211**, n = 1
**210**, n = 2

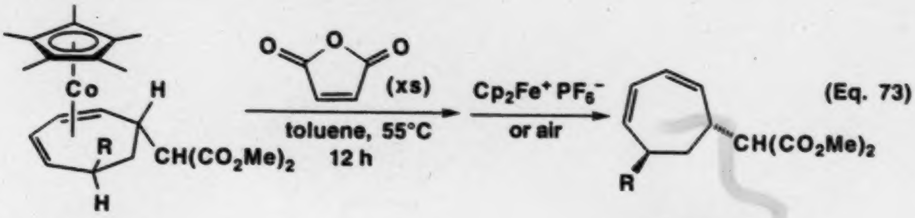
Demetallation of cycloheptadiene ligands with other substitution patterns was also assayed. Complex **194** is also readily demetallated by ferricenium oxidation to yield cycloheptadiene **212** as a colorless oil in 63% yield (Eq. **72**). No isomerization products of the diene are apparent in the $^1H$ NMR spectrum.



(Eq. 72)

**194** **212**

Even with rough optimization, the isolated yields of many cycloheptadiene products are moderate at best, although this is often unavoidable in similar oxidative decomplexation reactions.[138] Serendipitously, it has been found that maleic anhydride also effects this decomplexation and, for some substrates, returns higher yields. Treatment of the unsubstituted cobalt diene complex **192**, for example, with excess maleic anhydride, followed by either air or ferricenium oxidation yields the uncomplexed diene **206** (Eq. **73**) in nearly quantitative yield. Methylcycloheptadiene **207** is also obtained, albeit in only 47% unoptimized yield, by treatment of cobalt complex **195** with maleic anhydride, followed by air oxidation.



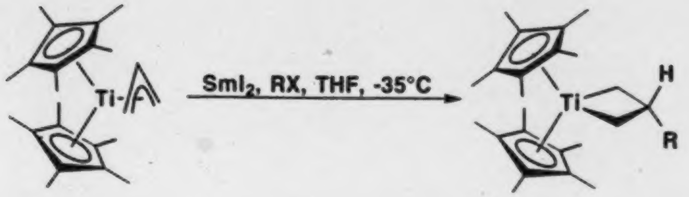
**192** R = H
**195** R = Me

**206** R = H, 92%
**207** R = Me, 47%

The mechanism of this fascinating transformation is unclear, but perhaps involves oxidation to a cobalt (II) oxidation state by maleic anhydride. The anhydride may somehow stabilize the intermediate cobalt (II) oxidation state, preventing decomposition. The fate of the maleic anhydride is unknown, but $(\eta^5\text{-}C_5Me_5)Co(NCMe)_3^{+2}$ is still recovered by addition of ferricenium hexafluorophosphate in acetonitrile in place of air oxidation. The fate of the metal upon air oxidation is also unknown. Much more study of this reaction is required to fully understand the mechanistic pathway(s).

### *D. Attempted Addition of Organic Radicals to Cationic Cycloheptadienyl Cobalt Complexes*

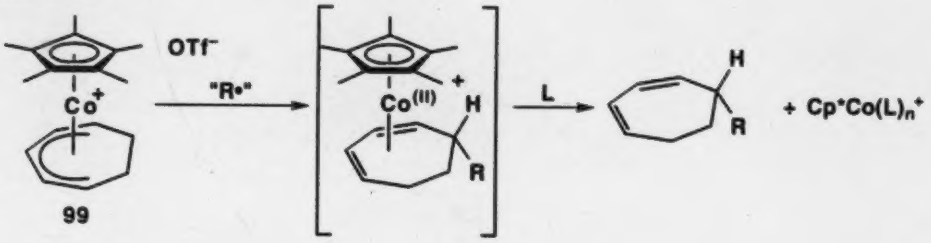
Addition of organic radicals to odd-electron organometallic complexes is still an area of expanding development.[141] The reaction of free radicals with titanium(III) allyl complexes, for example, has been reported to form titanacyclobutene complexes (Eq. 74).[141] However, addition of organic radicals to even electron, closed shell organometallic compounds has not received much attention.



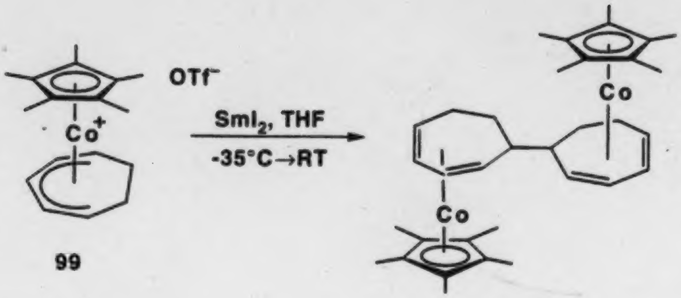
(Eq. 74)

Addition of a radical to cycloheptadienyl cobalt complex **99** would produce a cationic cobalt(II) diene complex, which may undergo a facile ligand displacement reaction (Scheme **38**). This process would effect ligand functionalization and decomplexation all in one step, representing an important conceptual advance. However, mixing the parent cycloheptadienyl complex **99** with AIBN in the presence of triphenylphosphine or acetonitrile in chlorobenzene solvent at 115°C does not appear to induce any reaction of the cobalt complex **99**.

**Scheme 38**



Other radical generating methods were also briefly investigated, particularly the generation of organic radicals from the reaction of $SmI_2$ with organic halides. However, the samarium reagent appears to react preferentially with the cobalt complex **99**, causing a one-electron reduction. This cobalt(II) intermediate undergoes further reaction to yield a pentane-soluble light orange complex tentatively identified as a ring-dimerization product by $^1H$ NMR spectroscopy (Eq. **75**). This type of ring dimerization product has been observed for a variety of metal complexes.[136]



99

(Eq. 75)

## III. Conclusions

We have demonstrated the conversion of cycloheptadienylcobalt complexes to coordinated cycloheptadienes by treatment with soft carbon nucleophiles. In particular, sodium malonate has been used as a reasonably selective nucleophile to form (malonyl)cycloheptadienecobalt complexes in high yield. Consecutive nucleophilic addition methodology has been demonstrated; this dramatically enhances the complexity of the cycloheptadiene ring, thereby increasing its synthetic value.

The (malonyl)cycloheptadienecobalt complexes have been converted to functionalized free organic cycloheptadiene compounds, completing the basic requirements for a synthetically viable process. Ferricenium hexafluorophosphate, a slightly unusual oxidant, has been shown to rapidly demetallate the ring system in moderate yields. Maleic anhydride has been shown remove the organic seven-membered ring from the cobalt complex, although this process requires further study.

# Chapter 4. Cobalt Cyclopentadiene Ring Expansion Reactions Forming Cycloheptadienyl Complexes. Carbon-Carbon Bond Activation of Cyclopentenyl Cobalt Intermediates.

## I. Introduction and Background

Selective carbon-carbon bond cleavage remains a relatively elusive but highly sought after goal of organometallic chemistry.[142] Hydrocarbons remain one of the most plentiful and economic sources of chemical feedstock; thus, the ability to directly utilize these compounds is of considerable importance. Carbon-hydrogen bond activation of alkanes is well known in both homogeneous and heterogeneous systems,[143] while alkane carbon-carbon bond activation is routinely achieved only by using heterogeneous catalysts.[144] However, such reactions usually require high temperatures or forcing conditions and lack selectivity. Alkanes, for example, can be cracked into smaller chains and undergo skeletal rearrangements under similar conditions using oxide-supported Pt catalysts.[144] Carbon-carbon bond activation in solution, however, remains a relatively rare occurrence.

One notable exception is the activation of alkane carbon-carbon bonds known to occur in superacids.[145] Gas phase reactions with "bare" atomic metal cations are also well known to result in the activation of carbon-carbon bonds, as well as carbon-oxygen, carbon-hydrogen, and carbon-halogen bonds.[146] Bond activation using such "reagents" is hardly unexpected, given the energy of ion-molecule collisions under the conditions employed. Such collisions impart excess internal energy of 40-60 kcal/mol to the system. This energy combined with the bond strength of the metal-carbon bond compensates for the breaking of the carbon-carbon bond.

In contrast, there are few examples of intermolecular carbon-carbon bond activation of unstrained molecules in solution. Heterogeneous catalysts as well as gas phase reactions are not generally selective in carbon-carbon bond activation reactions and most often give multiple products. In contrast, solution chemistry can in principle offer greater selectivity; only one active site is normally present in homogeneous systems, while several such sites typically exist in heterogeneous catalysts. Although the goal of catalytic carbon-carbon bond activation of unactivated hydrocarbons remains elusive, there are several homogeneous systems that now cleave either activated or coordinated carbon-carbon bonds.

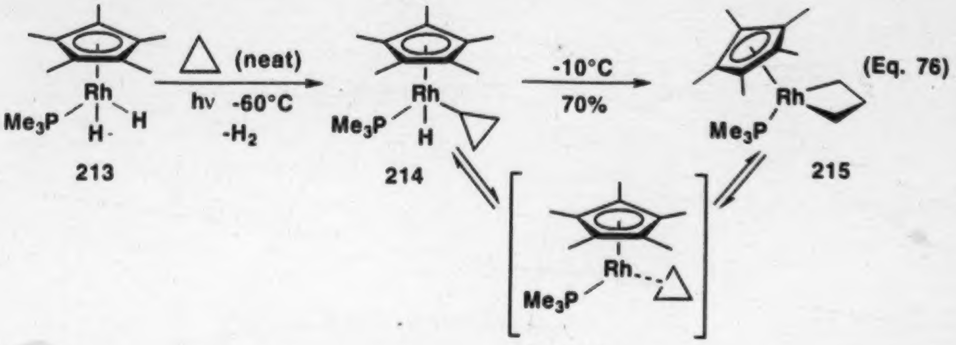
Unfortunately, in both heterogeneous and homogeneous systems, carbon-hydrogen activation often dominates, slowing or completely suppressing carbon-carbon bond activation.[144] One explanation for this phenomenon is that a high kinetic barrier to carbon-carbon bond activation exists arising from steric effects. Carbon-hydrogen bonds are on the periphery of the molecule and are much more readily accessible to external reagents. Carbon-carbon bonds, in contrast, are generally considered to be sterically less accessible to large metal complexes. Often in cases where carbon-carbon bond activation occurs, kinetically faster but reversible carbon-hydrogen activation is seen as well. The driving force for this type of reactivity is likely due to the irreversible nature of the carbon-carbon bond activation process. In the carbon-carbon bond activation product, β-hydrogen elimination is often kinetically faster than the reverse carbon-carbon reductive elimination, resulting in an effectively "irreversible" carbon-carbon activation process.

Other reasons for the predominance of carbon-hydrogen activation may be attributed to thermodynamic factors. The strength of the metal-hydrogen and metal-carbon bonds relative to the carbon-hydrogen or carbon-carbon bonds determines the thermodynamically most stable product. Carbon-carbon bond activation reactions have been estimated to be endothermic by 25 kcal/mol.[147] Other estimates, however, conclude that carbon-carbon bond activation reactions can be exothermic.[148] In all likelihood, the thermodynamic situation is highly dependent on both the particular metal template and the organic substrate.

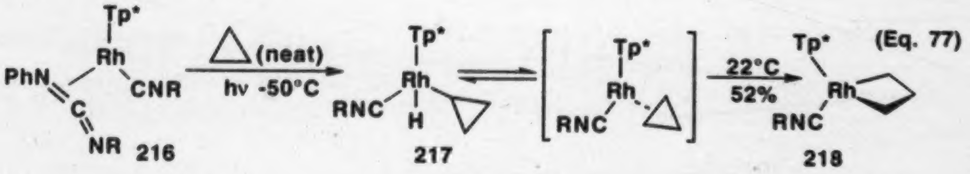
## A. *Carbon-Carbon Bond Activation of Strained Small Rings*

Cyclopropane systems have been known to undergo facile metal-assisted ring opening reactions for some time.[149] The general chemistry of cyclopropanes, cyclopropenes and methylenecyclopropanes, including the carbon-carbon bond activation chemistry of strained ring systems has been reviewed extensively.[30a,150] More recent work is focused on catalytic carbon-carbon bond activation of cyclopropanes, although the most interesting chemistry is seen in the few reported examples of carbon-carbon bond activation combined with further transformations.[151] For example, a variety of molecules insert into ring-opened cyclopropanes, including $CO_2$ and $HSiR_3$, giving lactone or open-chain silane products.[151a,d] Cyclopropane systems involved in formal [3 + 2] cycloaddition reactions with unsaturated hydrocarbon substrates catalyzed by transition metals have also been heavily studied.[30a,54,69-71]

Bergman's studies on the carbon-hydrogen and carbon-carbon bond activation of cyclopropane by rhodium complexes have also shown that conditions sometimes favor the thermodynamic carbon-carbon activation product over a kinetic carbon-hydrogen activation product (Eq. **76**).[143] An unsaturated rhodium system, generated from dihydride **213** by the low temperature photolytic loss of dihydrogen in neat cyclopropane, initially reacts with cyclopropane to form the kinetic carbon-hydrogen activation product: cyclopropyl hydride **214**. This complex rearranges by carbon-carbon bond activation at higher temperature to form rhodacyclobutane **215**. This process is proposed to occur by a reductive elimination reaction in the cyclopropyl hydride complex, generating an intermediate cyclopropane complex. The cyclopropane complex can either undergo carbon-hydrogen activation, returning to the cyclopropylmetal hydride complex **214**, or carbon-carbon bond activation, forming the thermodynamically more stable rhodacyclobutane complex **215**.


Rh
Me3P
H
213
(neat)
hν -60°C
-H2
Rh
Me3P
H
214
-10°C
70%
Rh
Me3P
215
(Eq. 76)
Rh
Me3P

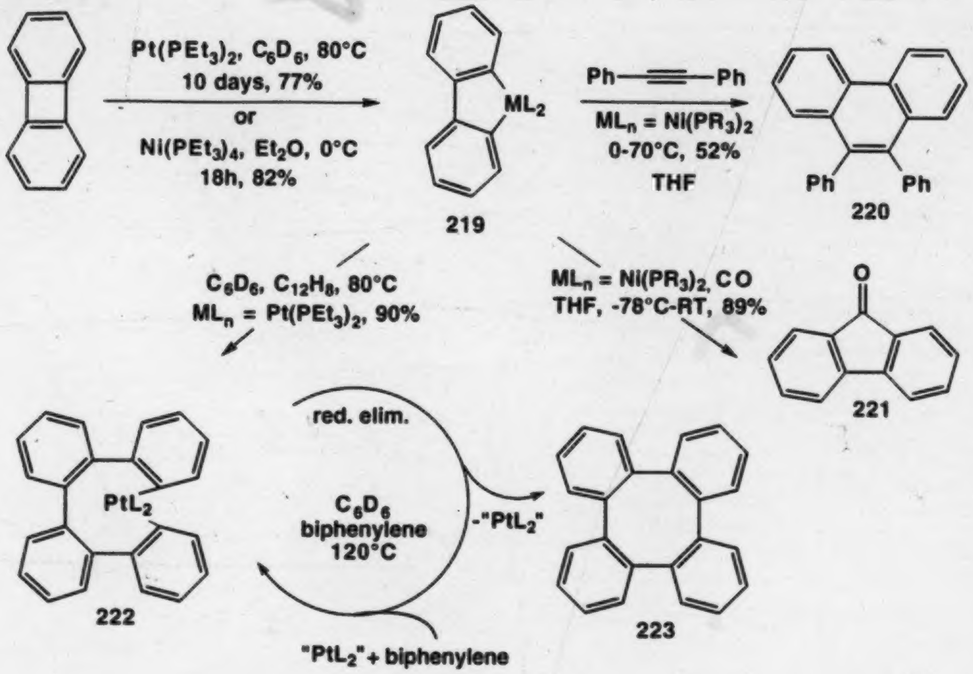
Other, more recent, studies in Tp*Rh (Tp* = tris(3,5-dimethylpyrazolyl)borate) chemistry parallel this work (Eq. 77). Jones has demonstrated that Tp* rhodium cyclopropyl hydride complex **217** is formed by carbon-hydrogen activation of cyclopropane in the low temperature photolysis of carbodiimide complex **216**.[152] Upon warming to room temperature, the cyclopropyl hydride **217** rearranges via carbon-carbon bond activation to yield rhodacyclobutane **218** as the thermodynamic product. This process is also thought to involve the carbon-carbon bond activation of an intermediate cyclopropane complex.


Tp*
Rh
PhN
CNR
C
NR
216
(neat)
hν -50°C
Tp*
Rh
RNC
H
217
Tp*
Rh
RNC
22°C
52%
Tp*
Rh
RNC
218
(Eq. 77)

The activation of carbon-carbon bonds in cyclobutane ring systems has been much less widely studied, although the ring strain energies of $C_3H_6$ and $C_4H_8$ are similar, estimated to be 27.5 and 26.5 kcal/mol, respectively.[150c] Flood has shown that a (1-methylcyclobutyl)methyl complex of platinum undergoes ring opening via β-alkyl elimination to an intermediate 4-methyl-pent-4-en-1-yl complex, which eventually rearranges to form substituted allyl complexes. Isotopic labeling studies demonstrate that cyclobutenylmethyl complexes are formed and consumed in rearrangements of 4-penten-1-yl complexes.[153] Other isolated examples include ring expansion reactions of iron tetramethylcyclobutadiene complexes,[154] a rhodium-mediated successive ring expansion of a spiro[2.3]hexanone to a cyclopentene ring,[155] and the rhodium-mediated carbon-carbon bond activation of the cyclobutane ring of a (cyclobutenyl)methyl ligand, a process very similar to that described by Flood.[156] Coordinated cyclobutyne ligands have also been reported to undergo carbon-carbon bond activation reactions in cluster compounds.[157] All of these examples are proximity-driven β-carbon elimination reactions; the activation occurs primarily because the carbon-carbon bond is constrained by coordination to be near the low-valent metal.

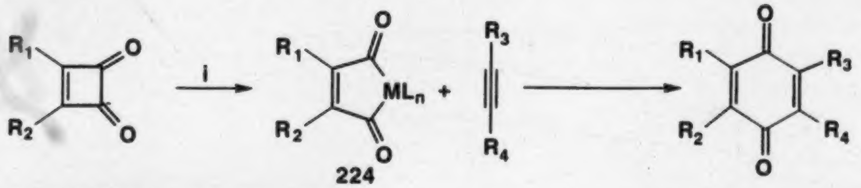
Most further examples also appear to first involve coordination of the substrate, followed by carbon-carbon bond cleavage. Activation of the carbon-carbon bond of biphenylene, for example, is relatively facile and has been known for some time.[158] This constitutes one of the very few general carbon-carbon bond activation reactions of four-membered rings. Several metal complexes will activate this strained carbon-carbon bond, forming biphenyl-2,2'-diyl complexes **219** in high yield.[159] Metal carbonyl clusters are also known to effect this transformation.[160] The insertion of small molecules such as CO or diphenylacetylene into the nickel-carbon bond of **219** has been reported, generating fluorenone **221** or diphenylanthracene **220**, respectively (Scheme **39**).[161] Jones has recently reported the development of a catalytic carbon-carbon bond activation/hydrogenation reaction of the carbon-carbon bond in biphenylene to produce biphenyl.[162] Dimerization of the biphenyl-2,2'-diyl complex **219** to a cyclooctatetraene system **223**[163] is known and very recently a catalytic variation of this reactivity pattern has been reported.[162] Treatment of the isolable intermediate **219** with excess biphenylene leads to formation of a 2,2'-tetraphenylene complex (**222**), which has been identified as the catalyst resting state. Further heating of **222** with biphenylene forms tetraphenylene (**223**) and regenerates the biphenyl-2,2'-diyl complex **222**.

Scheme 39


Pt(PEt3)2, C6D6, 80°C
10 days, 77%
or
Ni(PEt3)4, Et2O, 0°C
18h, 82%
ML2
219
Ph——Ph
MLn = Ni(PR3)2
0-70°C, 52%
THF
Ph
Ph
220
C6D6, C12H8, 80°C
MLn = Pt(PEt3)2, 90%
MLn = Ni(PR3)2, CO
THF, -78°C-RT, 89%
O
221
PtL2
222
red. elim.
C6D6
biphenylene
120°C
-"PtL2"
"PtL2"+ biphenylene
223

Liebeskind[24,164] has developed a *general* synthesis of quinones based on the carbon-carbon bond activation of cyclobutenediones, an activation reaction that had earlier been reported by both Kemmitt and Herrera.[165] The initial carbon-carbon bond activation provides an isolable maleoyl- or phthalolymetal complex, **224**, which undergoes an insertion reaction with an alkyne to provide the final quinone or naphthoquinone (Scheme **40**). This reactivity pattern has been expanded to include the carbon-carbon bond activation of the simpler cyclobutenones, providing phenols from the insertion with alkynes.[24,164f,g]

Scheme 40

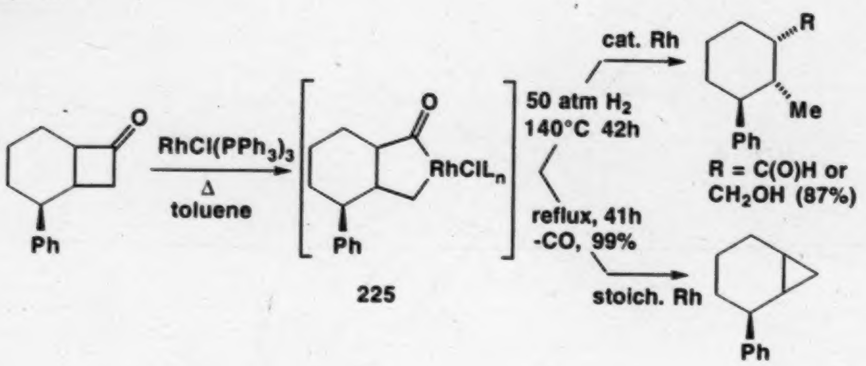


i) $Fe(CO)_5$, $C_6H_6$, hν, 48h, 83% or
$ClCo(PPh_3)_3$, $C_6H_5Cl$, 40°C,
24h, 92%
$R_1$, $R_2$ = Me, $(-CH_2-)_4$, or benzo
$R_3$, $R_4$ = alkyl, H, Ph, TMS, $CO_2Et$, OEt

$ML_n$ = $Fe(CO)_4$, 100°C, 6h, 75-95%
$ML_n$ = $CoCl(PPh_3)_2$, $AgBF_4$, 100°C, 3h,
65-90%

Murakami has shown that unsaturated rhodium complexes perform a variety of transformations on strained ring ketones by carbon-carbon bond activation pathways.[155,166] Decarbonylation of cyclobutanones is readily accomplished with a stoichiometric amount of $RhCl(PPh_3)_3$, which yields cyclopropane products (Scheme **41**). To a lesser extent, this process also works on some larger ring cyclic ketones.[166] The driving force in this reaction is likely due not to relief of ring strain, but rather to the formation of the thermodynamically very stable $Rh(CO)Cl(PPh_3)_2$. Metal-mediated decarbonylation of ketones by various rhodium complexes, especially $ClRh(PPh_3)_3$, has been known for some time.[167] A catalytic carbon-carbon bond activation/hydrogenation process has also been developed, transforming cyclobutanones into open-chain alcohols or aldehydes, albeit under different conditions (Scheme **41**).[166] The aldehyde presumably reacts further under the reductive reaction conditions to produce the alcohol, although production of the aldehyde can be made partially selective by using a lower amount of catalyst. The overall process is accomplished using a high pressure of $H_2$ in order to trap the product of carbon-carbon bond activation (**225**) before decarbonylation occurs. More recently, consecutive double carbon-carbon and carbon-carbon/carbon-oxygen bond cleavage reactions in strained bicyclic ring systems have been reported.[155,166c] A number of palladium-catalyzed ring cleavage reactions involving cyclobutanols have been reported recently.[166d]

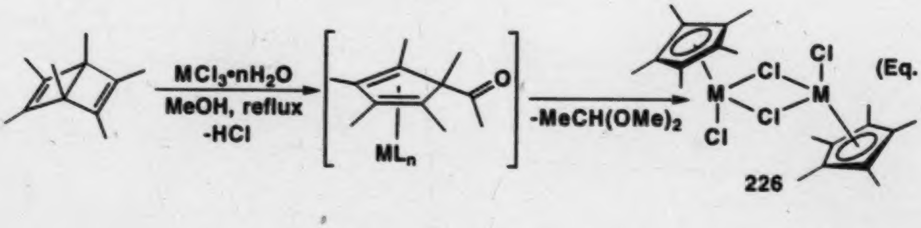
Scheme 41



RhCl(PPh$_3$)$_3$
Δ
toluene
O
Ph
RhClL$_n$
225
50 atm H$_2$
140°C 42h
cat. Rh
R
Me
Ph
R = C(O)H or CH$_2$OH (87%)
reflux, 41h
-CO, 99%
stoich. Rh
Ph

### *B. Carbon-Carbon Activation Driven by Ligand Aromaticity*

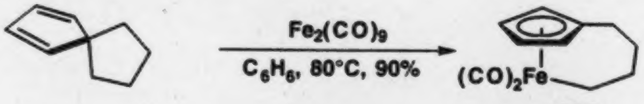
Although the relief of ring strain is a strong driving force in carbon-carbon bond activation reactions, other strategies have also been developed. A large amount of work has been devoted to the development of systems in which carbon-carbon bond activation is driven by the aromatic stabilization energy in the products formed from carbon-carbon bond activation. Additional stabilization is provided by the thermodynamic stability provided by the metal complex. One classical example is the rhodium trichloride or iridium trichloride mediated conversion of hexamethyldewarbenzene to stable pentamethylcyclopentadienyl metal complexes **226** (Eq. **78**).[168] The final step involves carbon-carbon activation of the cyclopentadiene-acyl bond. King has further studied the chemistry of acetyl pentamethylcyclopentadiene with transition metal complexes and reports selective carbon-carbon bond activation of the ring-acetyl bond, again forming pentamethylcyclopentadienyl metal complexes.[169]



MCl$_3$•nH$_2$O
MeOH, reflux
-HCl
O
ML$_n$
-MeCH(OMe)$_2$
M
Cl
Cl
Cl
Cl
M
226

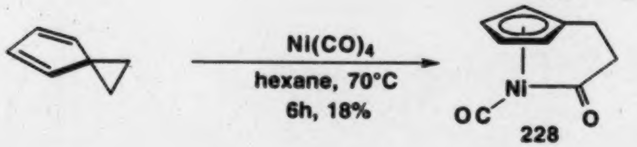
(Eq. 78)

Similar chemistry is seen when molybdenum, tungsten, iron or nickel carbonyl complexes react with spirocyclic cyclopentadienes (Eqs. **79**, **80**). Eilbracht has reported facile carbon-carbon bond activation of these [4.n]spiroalkadiene compounds in a reaction presumably driven by the aromaticity of the cyclopentadienylmetal product.[170] Generally, π-cyclopentadienyl metal σ-alkyl complexes **227** are formed from direct carbon-carbon bond activation, but using $Ni(CO)_4$, σ-acyl complexes **228** are formed from CO insertion into the intermediate σ–alkyl complex. Green has seen analogous reactivity when molybdenum atoms are condensed with spiro[2.4]hepta-4,6-diene.[171] Other groups describe similar reactivity for the reactions of metal complexes with spirocyclic hydrocarbon compounds.[172]



**227**

(Eq. 79)



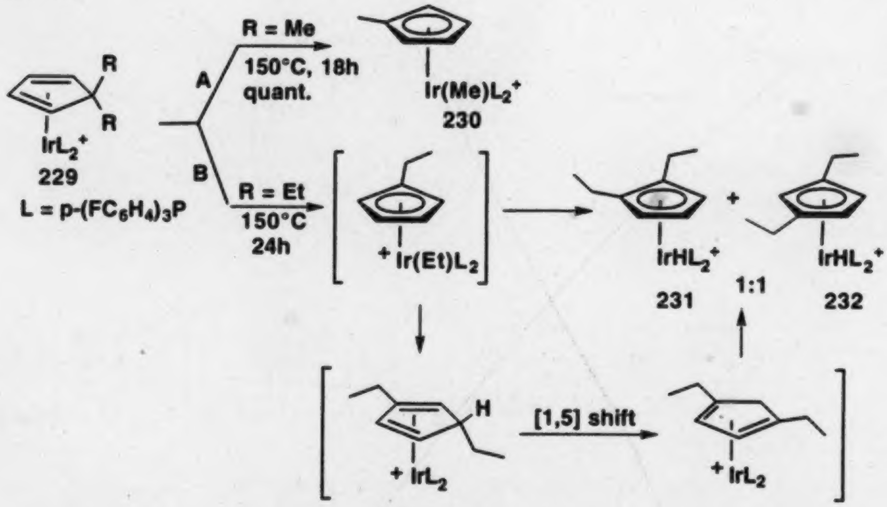
**228**

(Eq. 80)

Crabtree has reported unusual carbon-carbon bond activation reactions using iridium complexes of 1,1-dialkylcyclopentadienes (Scheme **42**).[173] These reactions appear to be highly dependent on the nature of the alkyl groups on the ring. 1,1-Dimethylcyclopentadiene complex **229** undergoes straightforward carbon-carbon bond activation of the *endo* methyl group (as determined from NOE measurements), forming complex **230** (Path **A**, Scheme **42**). With other alkyl groups, a variety of rearrangements are seen. Carbon-carbon bond activation still presumably occurs to give an analogous intermediate, $[(EtCp)Ir(Et)L_2]^+$, which is unstable with respect to further rearrangement. The ethyl group migrates back to different carbon atom on the ring instead of undergoing reductive elimination of ethane or β-hydrogen elimination. Carbon-hydrogen activation of the intermediate 1,*n*-diethyl cyclopentadiene complex forms the final 1,2- and 1,3-

diethylcyclopentadienyl complexes **231** and **232**, observed in about a 1:1 ratio. The mixed alkyl system, 1-ethyl-1-methylcyclopentadiene, when complexed to the iridium center yields a 3:1 mixture of complexed cyclopentadiene isomers, with the *endo*-methyl isomer as the major product. Thermolysis of this complex under similar conditions causes carbon-carbon bond activation of the *endo*-alkyl group. Green has reported the similar carbon-carbon bond activation of an *endo*-ethylcyclopentadiene ligand in a molybdenum complex.[173c]

**Scheme 42**

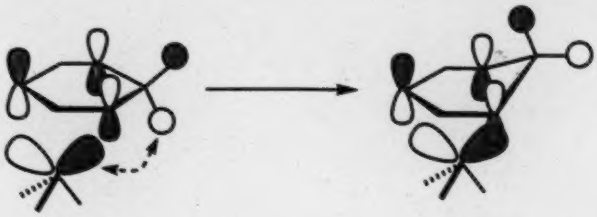


These reactivity patterns may be rationalized by considering that the Ir-Me bond is stronger than the Ir-Et bond. Carbon-carbon bond activation in **229** (R = Et) yields an intermediate $[(EtCp)Ir(Et)L_2]^+$, which is unstable with respect to further rearrangements. In contrast, carbon-carbon bond activation of **229** (R = Me) produces a stable, isolable product, $[(MeCp)Ir(Me)L_2]^+$ (**230**). When R = Et, this intermediate undergoes reductive coupling of the ethyl group and the Cp ligand to form a diethylcyclopentadiene ligand. Crabtree proposes a [1,5]-hydride shift on the Cp ring of this newly formed intermediate, placing a hydrogen *endo* to the metal; this may occur in the coordinated fragment, or the diene may first dissociate, undergo a [1,5]-hydride shift, and then recoordinate. Carbon-hydrogen bond activation provides the final hydride complexes **231** and **232**. The instability of the Ir-Et bond in this system can also be seen in the related complex $[CpIr(Et)L_2]^+$, L = *p*-$(FC_6H_4)_3P$, which also rearranges at 80°C to form an ethylcyclopentadienyl hydride complex.[173b]

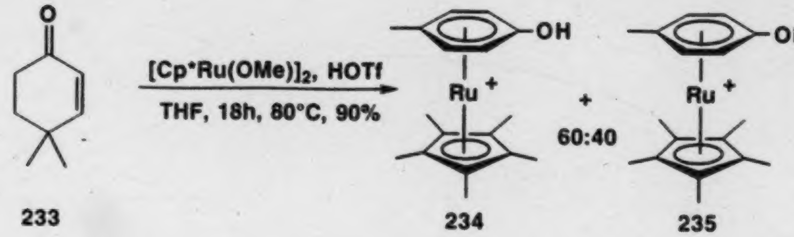
Other cases where carbon-carbon bond cleavage is competitive with carbon-hydrogen activation have also been observed. Carbon-hydrogen activation of methylcyclopentadiene is commonly used for the synthesis of methylcyclopentadienyl complexes. Jones has seen small amounts of competitive carbon-carbon bond activation of this synthon in certain rhenium systems.[174a] Similar to King's work,[169] Hughes has determined that up to 23% of the reaction between $C_5Me_5H$ and $Mn_2(CO)_{10}$ proceeds via carbon-carbon bond activation to give $(\eta^5\text{-}C_5Me_4H)Mn(CO)_3$ as opposed to the predicted carbon-hydrogen activation, which yields $(\eta^5\text{-}C_5Me_5)Mn(CO)_3$.[174b]

In contrast to the 1,1-dialkylcyclopentadiene systems, there are relatively few examples of carbon-carbon bond activation of 1,1-dialkylcyclohexadienyl derivatives, despite the ultimate formation of a coordinated aromatic ring. Crabtree was unable to induce carbon-carbon bond activation of coordinatively saturated 6,6-dimethylcyclohexadienyl iridium complexes.[173b] Wolczanski has shown that either oxidation to an odd-electron complex or generation of an unsaturated complex is required to accomplish carbon-carbon bond activation in (4,4-dimethylcyclohexadienyl)-ruthenium complexes, which then form stable $\eta^6$-toluene complexes, but only under harsh conditions.[175] Based on molecular orbital calculations on cyclohexadienyl metal systems, Hoffman has concluded that carbon-hydrogen or carbon-carbon activation of these systems is strongly disfavored.[175d] This is the result of an secondary antibonding interaction between the metal and the *endo* methylene hydrogen or carbon, which causes the methylene to significantly bend away from the metal, rendering the *endo* hydrogen or *endo* carbon inaccessible (Figure **13**).

**Figure 13**. MO Interactions for Cyclohexadienyl Metal Complexes

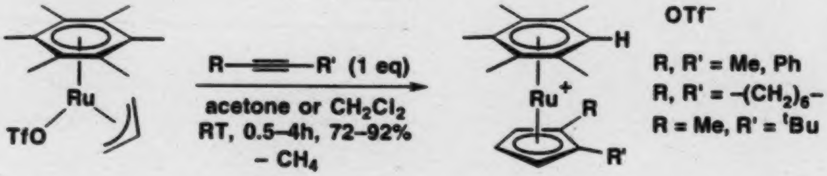


Chaudret has reported a complex cascade of reactivity, including ruthenium mediated carbon-carbon bond activation of coordinated 6,6-dimethylcyclohexenones to yield stable ruthenium arene complexes (Eq. **81**).[176] The electrophilic $C_5Me_5Ru^+$ fragment, prepared from $[(\eta^5\text{-}C_5Me_5)Ru(OMe)]_2$ and triflic acid, has a high affinity for arene complexation, which is a useful feature for the carbon-carbon activation of dialkylcyclohexenes. This fragment, when allowed to react with 3-methylcyclohexene, forms primarily a toluene complex but also small amounts of a benzene complex from both carbon-hydrogen and carbon-carbon bond activation reactions, respectively. However, only a small amount of carbon-carbon activation is seen in cases where a competitive carbon-hydrogen activation pathway exists. To exploit this reactivity pattern more efficiently, the ruthenium fragment was treated with various 1,1-dialkylcyclohexene compounds to force a carbon-carbon activation to occur. For example, 4,4-dimethylcyclohexen-1-one **233** provides a mixture of 4-methylphenol ruthenium complex **234** and 4-methylanisole complex **235** in high yield (Eq. **81**). The use of this ruthenium fragment has been particularly effective in the selective aromatization of steroids by carbon-carbon bond activation of an angular methyl group.[176b,c] Itoh has seen a similar reactivity pattern in the cycloaddition reaction of $(\eta^5\text{-}C_5Me_5)Ru(\eta^4\text{-}1,3\text{-pentadiene})(Cl)$ with silver triflate and acetylene in $CH_2Cl_2$; a small amount of $(\eta^5\text{-}C_5Me_5)Ru(C_6H_6)^+$ $OTf^-$ is formed via carbon-carbon activation and methane loss after the initial [4 + 2] cycloaddition.[176e]



(Eq. 81)

Certain ruthenium complexes formed during an initial [3 + 2] allyl/alkyne cycloaddition undergo a further interesting reaction: carbon-carbon bond activation of the coordinated hexamethylbenzene ligand, which releases methane and forms a pentamethylbenzene complex (Eq. **82**).[120,177] No trace of hexamethylbenzene products are observed. This remarkably facile example of carbon-carbon activation proceeds in good yield at ambient temperature, in sharp contrast to the long periods of heating required in Chaudret's system.[176] This process appears to be driven by the steric strain induced by the six mutually buttressed methyl groups of the hexamethylbenzene. Astruc has reported that the Lewis acid induced ligand exchange reaction of hexamethylbenzene with the cyclopentadienyl ligand in ruthenocene complexes proceeds with extensive demethylation of the hexamethylbenzene.[178] Although this phenomenon was originally attributed to the influence of $AlCl_3$ in the reaction mixture prior to complexation, later experimental work demonstrated that this carbon-carbon bond activation is attributed to the interaction with the ruthenium center. Additionally, de-ethylation of the hexa*ethyl*benzene analogue was shown to occur after coordination of the arene ligand to yield ($\eta^5$-$C_5H_5$)Fe($\eta^6$-pentaethylbenzene), from loss of a single ethyl group.[178]

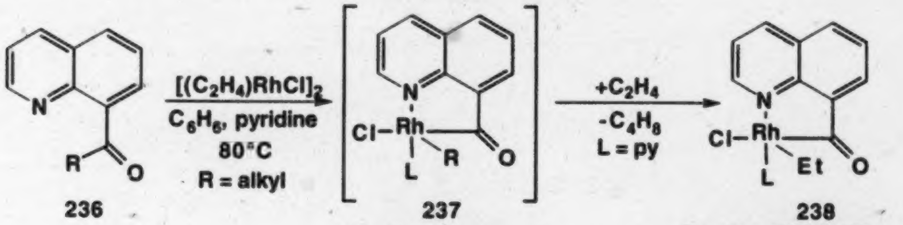


(Eq. 82)

## *C. Oxidative Carbon-Carbon Activation by Forced Proximity to the Metal Center*

Another major strategy for activation of carbon-carbon bonds is to effect the forced proximity of carbon-carbon bonds to a low valent metal center. The proximity creates a high local concentration of the "reactant" carbon-carbon bond at the metal center; as well, the carbon-carbon bond is often preferentially oriented toward the metal center, disfavoring competitive carbon-hydrogen activation. This lowers the kinetic barrier to carbon-carbon activation and enhances the rate of the reaction. It should be noted that in many such cases, reversible carbon-hydrogen activation also occurs, but the carbon-hydrogen activation product retains a sterically bulky ligand which experiences strong repulsive interactions with the metal center. Thus, carbon-carbon activation in such cases can be both kinetically and thermodynamically enhanced, as the metal center attempts to reduce the interaction with the proximal carbon-carbon bond.

In contrast to some of the previously illustrated examples, where the activation process is best viewed as a β-carbon elimination reaction (Section D), the following reactions are clearly better described by an oxidative addition process. Suggs has observed carbon-carbon bond activation of 8-quinolinyl alkyl ketones **236** using $[(C_2H_4)RhCl]_2$ in benzene solvent (Eq. **83**).[179] Ethylene is easily displaced in this complex and the subsequent coordination of the quinoline nitrogen atom to the rhodium center places a carbon-carbon bond of the ketone near the unsaturated rhodium center. Carbon-carbon bond activation occurs oxidatively to form an insoluble polymer, which can be solubilized by added pyridine, forming acyl alkyl complexes **237** (R = Ph, Me, $C_2Ph$, benzyl). Interestingly, if the R group has a β-hydrogen atom (R = Bu, CH(Me)Ph, cyclohexyl), complex **237** is not observed; instead, the ethyl complex **238** is the sole product. β-Hydride elimination from complex **237** is apparently facile and the newly formed alkene is lost, creating an intermediate acyl hydride complex. This intermediate is highly reactive and undergoes insertion of the ethylene remaining from the $[(C_2H_4)RhCl]_2$ to form the rhodium acyl ethyl complexes **238**. The energy barrier to reductive elimination of the acyl/alkyl pair must be larger than that to β-H elimination in order to see this exchange, although another rationale is that the reaction is reversible. Jun has recently developed a catalytic version of this process, which exchanges the alkyl group in aromatic ketones with a different alkyl group.[179g]

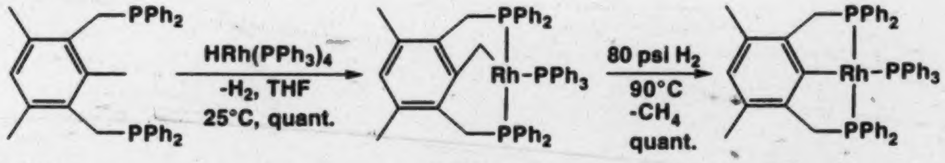

N
R
O
[(C2H4)RhCl]2
C6H6, pyridine
80°C
R = alkyl
N
Cl–Rh
L
R
O
+C2H4
-C4H8
L = py
N
Cl–Rh
L
Et
O

**236** **237** R = Me, Ph, Et, $C_2Ph$, $CH_2Ph$ **238** R = Bu, CH(Me)Ph, $CMe_2Ph$, cyclohexyl

(Eq. 83)

Milstein has expended considerable effort to develop systems that effect carbon-carbon activation of bonds in proximity to a metal center by ligand complexation.[180] Coordination of the phosphine arms of diphosphine **239** to $HRh(PPh_3)_3$ orients the methyl group of the ligand toward the rhodium center (Scheme **43**). Rapid, reversible carbon-hydrogen activation to form **240** is observed initially; however, when the complex is heated under a hydrogen atmosphere, carbon-carbon bond activation and subsequent loss of methane occur to give the metal aryl complex **241**.

**Scheme 43**

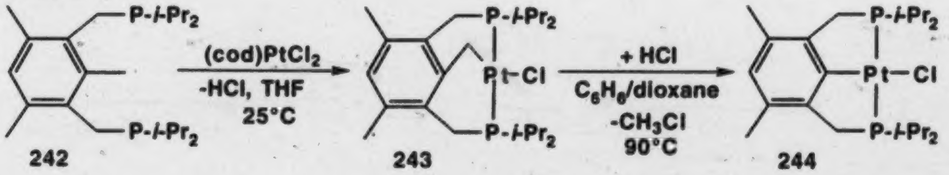

PPh2
PPh2
HRh(PPh3)4
-H2, THF
25°C, quant.
PPh2
Rh-PPh3
PPh2
80 psi H2
90°C
-CH4
quant.
PPh2
Rh-PPh3
PPh2

**239** **240** **241**

Milstein has also shown that the methyl group from these carbon-carbon activation reactions can be transferred to other reagents: a reaction initially reported by van Koten.[180] Addition of $HSi(OEt)_3$ to **240** followed by thermolysis at 100°C yields $CH_3Si(OEt)_3$ and **241**. The proposed pathway first involves H-Si oxidative addition to the rhodium center, forming a methylene silyl hydride. This is followed by C-Si reductive elimination to form a rhodium hydride intermediate. Carbon-carbon activation and carbon-hydrogen reductive elimination yield the final products, **241** and $CH_3Si(OEt)_3$.

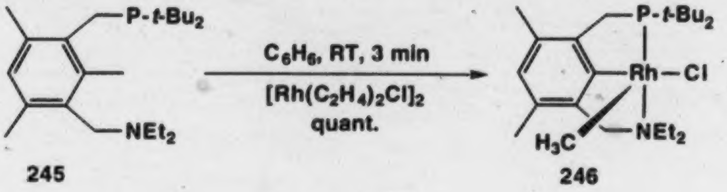
Other transformations using variations of this template have been reported.[180] Reaction of the analogous ethyl-substituted ligand with $HRh(PPh_3)_3$ produces ethane from carbon-carbon bond activation of the aryl-ethyl bond, another indication of the crowded geometry about the metal center. It is apparent that the large difference in the carbon-carbon bond strengths between the aryl-ethyl and the benzylic bond of the ethyl group has little effect. The close proximity and orientation of the carbon-carbon bond relative to the metal center are more important factors than the bond strength in this particular example. Due to the larger steric constraints, the $CH_2$-$CH_3$ bond cannot approach the metal center and is left intact. Similarly, the reaction of (1,5-cod)$PtCl_2$ with 2,4-bis(diisopropylphosphinomethyl)mesitylene (**242**) yields the platinum chloride complex **243** (Scheme **44**). This platinum complex loses chloromethane upon thermolysis in the presence of excess HCl (10 equiv, 82°C, 45 min, benzene-dioxane), leading to the formation of the platinum chloride complex **244**.

**Scheme 44**



Carbon-carbon bond activation has been shown to be both thermodynamically and kinetically preferred in some systems (Eq. **84**).[180] No carbon-hydrogen activation product is seen by $^1H$ NMR spectroscopy when $[Rh(C_2H_4)_2Cl]_2$ reacts with the ligand

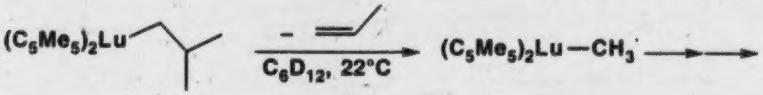
**245**; only the product of carbon-carbon activation (**246**) is observed. The conclusion drawn from this observation is either that carbon-carbon bond activation is kinetically preferred or that carbon-hydrogen activation is reversible and too fast to be observed on the NMR spectroscopic time scale. Activation of the very strong aryl-$CF_3$ bond by similar methodology has also been reported, another indication that this process is not greatly dependent on the strength of the carbon-carbon bond.[180]



(Eq. 84)

### *D. β-Carbon Elimination Reactions*

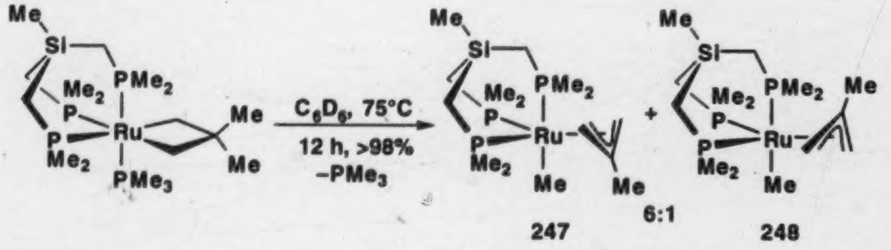
One very common transformation of metal alkyl complexes is β-hydrogen elimination.[1,2] Only relatively recently has the analogous process of β-carbon elimination been observed, beginning with Watson's report of β-methyl elimination in $Cp^*{}_2Lu$(alkyl) complexes (Eq. **85**).[181] Soon thereafter, Flood observed a formal



(Eq. 85)

alkene insertion/β-alkyl elimination process using a (2,2-dimethyl-4-penten-1-yl)platinum complex, which was proposed to involve β-alkyl elimination from an intermediate (dimethylcyclobutyl)methyl complex.[153] Bercaw has proposed a similar process in the scandium-mediated isomerization of 1,4-pentadienes,[182] a process that has also been used to describe the nickel-mediated isomerization of 1,4-dienes.[183] Rearrangements of bis[(trimethylsilyl)methyl]platinum complexes appear to involve a β-carbon elimination, cleaving a C-Si bond forming $MePt(CH_2SiMe_2CH_2SiMe_3)L_2$ after rearrangement.[184] Cp*Cr(II)(dmpe)Me has been shown to favor β-alkyl elimination over β–hydride elimination in ethylene polymerization.[185] β-Methyl elimination has also been shown to be a chain-termination step in several $Cp^*_2MX_2$/MAO (M = Ti, Zr, Hf)-catalyzed alkene polymerization processes.[186] β-Alkyl elimination has been demonstrated to be competitive with β-hydrogen elimination as a chain-termination step in propene polymerization by permethylscandocene catalysts.[187] Marks has developed this β-alkyl shift process into a chain propagation pathway, polymerizing methylenecyclobutane and forming a polymer composed of acyclic monomer units.[188] This differs from traditional ring opening metathesis polymerization (ROMP) reactions in that β-alkyl elimination, not alkene metathesis, is the propagation step.[189]

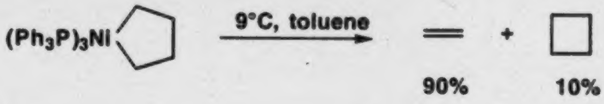
Bergman has recently demonstrated the first directly observable β-methyl elimination process; a dimethylmetallacyclobutane complex is transformed by carbon-carbon activation into *endo* and *exo* (2-methylallyl)(methyl)ruthenium complexes **247** and **248** upon thermolysis (Eq. **86**).[190] β-Alkyl elimination of a methyl group has



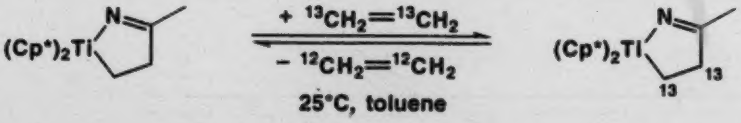
(Eq. 86)

previously been observed in related ruthenium oxametallacyclobutane complexes bearing both β-methyl and β-phenyl groups.[191] Interestingly, a similar series of carbon-hydrogen or carbon-carbon activation reactions and reductive eliminations transforms a neopentyl ligand into a ruthenium trimethylenemethane complex.[190b] β-Methyl elimination has also been recently reported in zirconium neopentyl complexes and reversible migratory insertion and β-alkyl elimination processes have recently been observed in alkylniobium complexes.[192,193] A ruthenium-mediated process has been shown to convert homoallyl tertiary alcohols into ketones via a β-allyl elimination reaction.[194a] Carbon-carbon bond activation of the phosphine ligand of $Os(H)_2(Cl)_2(P^iPr_3)_2$ has been observed.[194b]

Another common transformation, the oxidative coupling of two olefins at a transition metal center to yield a metallacyclopentane, has been shown to be reversible. Quite some time ago, Grubbs clearly demonstrated this β-alkyl elimination process, reporting that the decomposition of tris(triphenylphosphine)nickelacyclopentane yields ethylene as the major product, along with small amounts of butene and cyclobutane (Eq. **87**).[195] Whitesides had earlier reported that decomposition of an analogous complex, bis(pentamethylcyclopentadienyl)titanacyclopentane, also produces significant amounts of ethylene, presumably also by β-alkyl elimination.[196] Bercaw has studied the equilibrium between this titanacyclopentane complex and $(\eta^5\text{-}C_5Me_5)_2Ti(C_2H_4)$ under an ethylene atmosphere.[197] Current with these original reports, a rhodacyclopentane complex was also shown to produce small amounts of ethylene upon thermolysis.[198] Erker has reported that that bis(cyclopentadienyl)hafnacyclopentane undergoes β-carbon elimination at 90°C in aromatic solvents.[199] Negeshi has also shown that both bis(cyclopentadienyl)hafnacyclopentane and bis(cyclopentadienyl)zirconacyclopentane undergo ring opening β-alkyl elimination reactions in the presence of phosphines to produce $Cp_2M(C_2H_4)(PR_3)$ (M = Zr, Hf) complexes.[200] Marks has studied the thermochemistry of $Cp^*{}_2Zr$ and $Cp^*{}_2Hf$ complexes, including the formation of metallacyclopentane complexes.[201] Using $^{13}C$-labeled ethylene, Bercaw has demonstrated that bis(pentamethylcyclopentadienyl)azatitanacyclopentene complexes also undergo reversible β-alkyl elimination reactions (Eq. **88**).[202]



(Eq. 87)



(Eq. 88)

### *E. Miscellaneous Carbon-Carbon Bond Activation Reactions*

There are several recent examples of formal carbon-carbon bond activation reactions that are not readily classified. Electrochemically induced carbon-carbon bond activation of ancillary ligands, such as cyclooctatetraene, in transition metal complexes has been demonstrated.[203] Chemical reduction of organoboranes by one electron leads to ligand rearrangement by carbon-carbon activation.[204] Other unusual carbon-carbon activation reactions of coordinated ligands have been reported.[205,206] The activation of the sp-sp-hybridized carbon-carbon bond in butadiyne and poly-ynes by the $Cp_2Ti$ fragment has recently been reported.[207] The mechanism of the ruthenium-mediated carbon-carbon cleavage of terminal alkynes by primary amines and water to produce carbonyl compounds has recently been investigated.[208] Advances in the transition metal-mediated activation of alkene double bonds to produce carbonyl compounds have also recently been reported.[209]

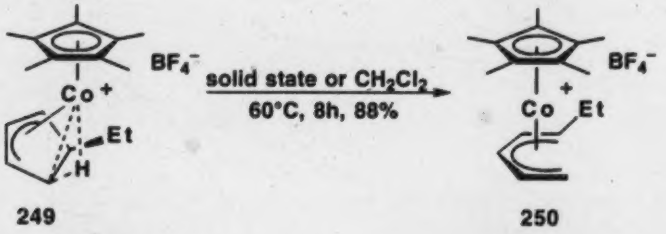
In spite of the relative abundance of carbon-carbon bond activation examples, the cleavage of completely unactivated carbon-carbon bonds by homogeneous complexes is still very rare. Sen has, however, reported carbon-carbon bond activation products from small chain alkanes in hydroxycarbonylation catalysis.[210] Suzuki has reported a ruthenium cluster that is capable of the carbon-carbon bond activation of cyclopentadiene, although the system is more commonly used for the activation of C-S bonds.[211] Earlier, Shapley had demonstrated cleavage of the triple bond of coordinated alkynes by a tungsten-triosmium cluster.[212]

Recent development of carbon-carbon activation processes has not been limited to homogeneous systems. For example, Basset has developed a silica-supported zirconium catalyst capable of cleaving carbon-carbon bonds under high hydrogen pressure, thus forming methane and ethane from higher olefins and dihydrogen.[213] Finally, carbon-

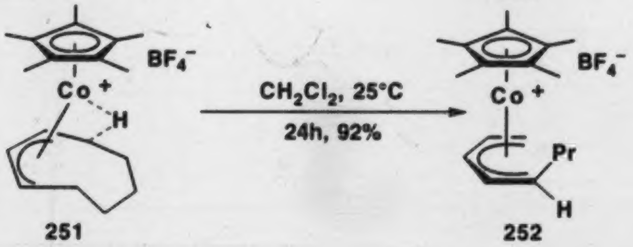
carbon bond activation of cyclobutane has recently been observed on a ruthenium surface.[214]

### *F. Carbon-Carbon Bond Activation in Electrophilic Cobalt Complexes*

Electrophilic cobalt complexes are known to activate carbon-carbon bonds under certain circumstances. Spencer has reported that the cationic Cp*Co(cyclopentenyl) complex **249**, with an agostic ground state, ring opens to the $\eta^5$-pentadienyl cation **250** upon thermolysis (Eq. **89**).[128] The analogous six-membered cyclohexenyl complex does not undergo a corresponding carbon-carbon activation, even upon prolonged thermolysis, but the cyclooctenyl complex **251** undergoes very facile ring opening at room temperature to give $\eta^5$-propylpentadienyl complex **252** (Eq. **90**).



(Eq. 89)

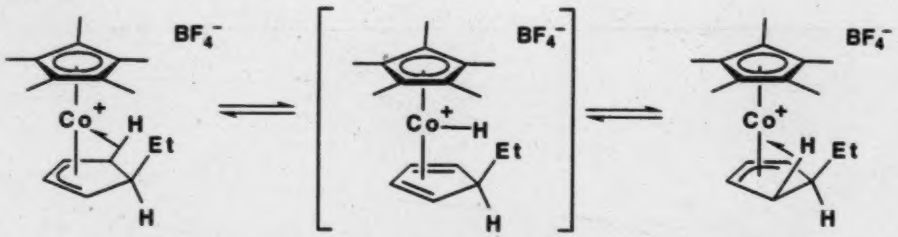


(Eq. 90)

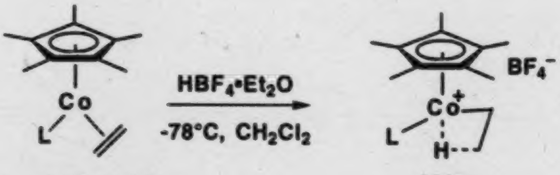
Both nominally unsaturated allyl complexes **249** and **251** are stabilized by agostic interactions, apparent from ${}^1J_{CH}$ values for the agostic carbon in **249**. This carbon appears as a doublet of doublets in the fully coupled ${}^{13}$C NMR spectrum, with ${}^1J_{CH}$ values of 74 and 157 Hz. The agostic hydrogen appears in the ${}^1$H NMR spectrum at -14.4 ppm (d, $J_{HH,gem}$= 25 Hz), values that are diagnostic for agostic complexes.[215] The ring opening reactions are presumably driven by the stabilization provided by the saturating $\eta^5$-pentadienyl fragment.

Carbon-hydrogen bond activation products in this system are not observed, likely because diene-hydride structures in this cobalt system are at higher energy than the allylic agostic structure. However, Spencer has shown that complexes **249** and **251** are highly fluxional, equilibrating between different agostic structures, illustrated for **249** in Scheme **45**. This reaction likely occurs by β-hydride elimination and re-insertion of the hydride to reform an isomerized agostic allyl complex.

**Scheme 45**



Brookhart and others have demonstrated that protonation of $C_5R_5Co(C_2H_4)(L)$ (L = ethylene or phosphine) with tetrafluoroboroic acid very easily forms the agostic ethyl complex **253**, demonstrating the relative instability of cobalt alkene hydrides (Eq. **91**).[216] Such complexes are reasonably active olefin dimerization and polymerization catalysts.



L = $C_2H_4$ or $PR_3$

**253**

(Eq. 91)

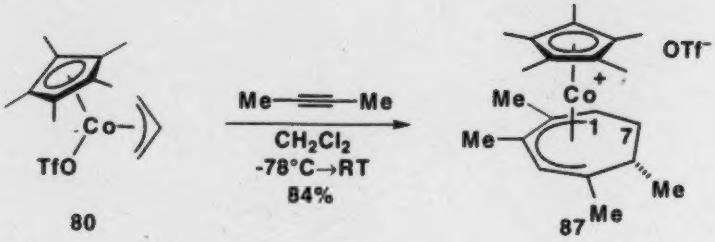
## II. Results and Discussion

As briefly discussed in Chapter 2, several [3 + 2 + 2] cobalt-mediated allyl/alkyne cycloaddition reactions produce cycloheptadienyl complexes with unexpected substitution patterns. While developing an explanation for these results, a separate project was created out of the discovery that facile carbon-carbon bond cleavage forms an integral part of this abnormal [3 + 2 + 2] cycloaddition process. While superficially related to the carbon-carbon activation of cyclopentenylcobalt complexes observed by Spencer, the mechanistic pathway determined for these transformations is clearly quite distinct. In this Chapter, the reactions of allyl templates with 2-butyne and potential mechanistic pathways are discussed. Although these cycloheptadienyl products superficially ressemble the products of the sequential [3 + 2 + 2] allyl/alkyne cycloaddition pathway, the following examples arise from distinct carbon-carbon bond activation reactions, as determined by the anomalous substitution patterns. In the subsequent Chapter, further development of the carbon-carbon activation pathway is described.

### A. *Anomalous [3 + 2 + 2] Cycloaddition Reactions Involving 2-Butyne*

The reaction of excess 2-butyne with many ($\eta^5$-$C_5R_5$)Co(allyl) complexes gives cycloheptadienyl products with substitution patterns that are not readily explained. Furthermore, slight changes in the substrate, such as replacing the allyl ligand with the 1-methylallyl ligand, cause dramatic differences in the structures of the reaction products.

The reaction of Cp*Co(allyl)(triflate) **80** with excess butyne ($CH_2Cl_2$, -78°C), for example, gives the unexpected complex **87** in very good (80-85%) yield (Eq. **92**).[88] This complex has been fully characterized by unambiguous spectroscopic and analytical techniques, as well as by conversion to well-characterized derivatives by hydride addition and deprotonation (see Scheme **14**, Chapter 2, page 36).[88]



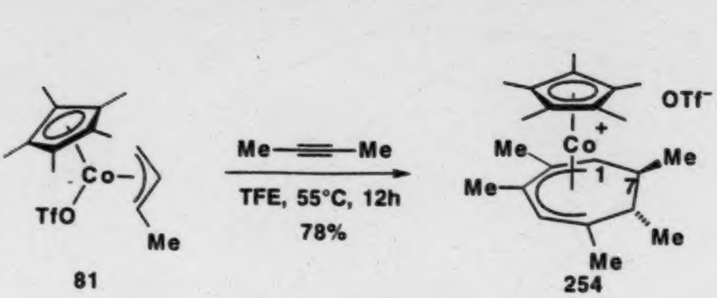
(Eq. 92)

Although clearly a cycloheptadienyl complex, the substitution pattern and methyl stereochemistry demonstrate that a straightforward [3 + 2 + 2] reaction does not take place. The appearance of a singlet at δ 5.10 ($H_4$) in the $^1H$ NMR spectrum indicates a proton on the pentadienyl fragment that is bordered on both sides by methyl groups. A doublet ($J$ = 6.8 Hz) at δ 0.99, integrating to three hydrogen atoms, is observed for the *exo* methyl group in complex **87**, which is shifted slightly upfield from the normal *endo* methyl groups, such as those observed in methyl- and dimethylcycloheptadienyl complexes **101** and **102**, which resonate at δ 1.11 and 1.05, respectively. The $H_{6endo}$ proton itself is dramatically shifted upfield to δ 0.75 from the normal range of about δ 2.0-1.6. The value of 9.5 Hz for the $J_{6endo\text{-}7endo}$ coupling constant is close to the standard value of about 6-9 Hz that is seen in other cycloheptadienyl complexes, indicating the methyl group is in an *exo* position. Note that, for the opposite stereochemistry, the value for this coupling constant is expected to be much smaller, *i.e.*, 0-4 Hz. Unfortunately, further conformational data are unavailable, due to the multiplet character of $H_{7exo}$ and $H_{6exo}$.

However, the reaction of other disubstituted alkynes, such as cyclooctyne, exclusively yields a "normal" product from a straightforward [3 + 2 + 2] allyl/alkyne cycloaddition reaction (Scheme **12**, Chapter 2, pp 33). Thus, with 2-butyne, some subtle change is in effect, altering the reaction pathway. Two disubstituted alkynes, diphenylacetylene and 4,4-dimethyl-2-pentyne, yield five membered rings exclusively in the reaction with allyl triflate complex **80**, indicating that coordination of the second alkyne may be much slower than cyclization to a five-membered ring in these cases.[88]

Several attempts were made to follow the course of the reaction of allyl triflate complex **80** with 2-butyne by low temperature $^1$H NMR spectroscopy, but no additional information could be obtained.[88] In some cases, a small amount of paramagnetic material is formed, a typical hazard in cobalt chemistry, obscuring all signals in the $^1$H NMR spectrum. However, in other cases, only the initial allyl and the final product can be seen, along with a small amount of a material tentatively assigned as the simple allyl alkyne complex. Although this type of intermediate has previously been isolated in related, but less reactive, iridium systems,[61,91] all attempts to isolate or trap the cobalt allyl/alkyne intermediate or the immediate product of insertion failed.

When the corresponding crotyl triflate complex **81** reacts with excess 2-butyne, albeit under quite different conditions (TFE, 55°C), a similar dark red cycloheptadienyl complex **254** is obtained in 78% yield after isolation and purification by flash chromatography (Eq. **93**). Under the more typical conditions used to form tetramethylcycloheptadienyl complex **87** ($CH_2Cl_2$, -78°C), the same pentamethylcycloheptadienyl complex **254** is formed, but in lower yield. The presence of a singlet ($\delta$ 4.91, $H_4$) in the $^1$H NMR spectrum indicates the hydrogen on the pentadienyl fragment is again flanked by methyl groups. Two methyl doublets are observed at upfield positions; the ring conformation dramatically affects the chemical shift of the 6-*endo* proton. This signal resonates at $\delta$ -0.12, an upfield shift of almost 0.9 ppm compared to complex **87**, the product from the corresponding reaction with allyl complex **80** and excess 2-butyne. The large number of methyl groups in the molecule apparently alters the conformation of the seven-membered ring; few direct comparisons of the respective $^1$H NMR spectra may be made. As previously seen in methyl- and dimethylcycloheptadienyl complexes **100** and **101** (Chapter 2), the crotyl compounds insert the alkyne to form an *endo* methyl group. In contrast, the rearrangement that forms complexes **87** and **254** generates an *exo* methyl group.



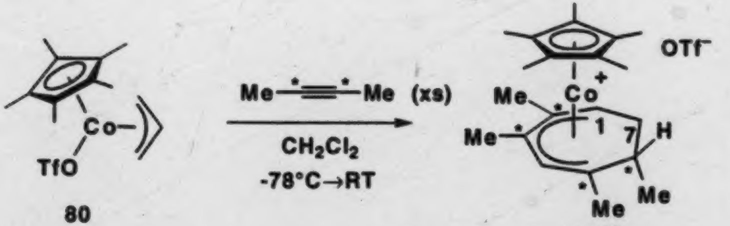
81 254

(Eq. 93)

In principal, this rearrangement could occur either by the shift of a methyl group on the skeletal framework or by a rearrangement of the carbon skeleton itself. Further, each transformation could occur either after cyclization to the seven-membered ring, or at some indeterminate intermediate step. These two processes, skeletal rearrangement or a methyl group shift, can potentially be distinguished by undertaking a labelling study to determine whether the methyl groups of 2-butyne maintain or change positions during the cycloaddition.

In order to conclusively evaluate the possibility of a methyl migration in these rearrangements, the previously unknown doubly $^{13}$C-labeled 2-butyne ($CH_3{}^{13}C{\equiv}{}^{13}CCH_3$) was synthesized. Commercial doubly $^{13}$C-labeled acetylene was doubly deprotonated using BuLi in diethyl ether at -78°C, and the resulting insoluble $Li^{13}C{\equiv}{}^{13}CLi$ was dried *in vacuo*. The salt was treated with dimethylsulfate in HMPA at 11°C and after all the insoluble $Li^{13}C{\equiv}{}^{13}CLi$ had dissolved, the reaction was allowed to stir for an additional 30 min. The entire system was then frozen (-196°C) and degassed. The doubly $^{13}$C-labeled 2-butyne was isolated by vacuum transfer, separating the volatile product from the relatively involatile solvents. The $^1$H NMR spectrum shows a triplet at $\delta$ 1.72 ($^2J_{CH} = {}^3J_{CH} = 3.0$ Hz) and the $^{13}$C NMR spectrum of the product shows a single labeled carbon at $\delta$ 74.6. The methyl (unlabeled) carbons were not located above baseline noise.

The reaction of the allyl triflate complex **80** with an excess of the doubly $^{13}$C labeled 2-butyne gives the labeled $\eta^5$-cycloheptadienyl complex **87**-$^{13}C_4$ (Eq. **94**). Due to the extensive number of ${}^2J_{CH}$ and ${}^3J_{CH}$ couplings to the labeled carbon atoms, all signals in the ${}^1H$ NMR spectrum are transformed into unresolved multiplets. Chemical shift values of these multiplets, however, are consistent with the unlabeled complex, indicating that the same product is formed. The ${}^{13}C$ NMR spectrum indicates that a single quadruply labeled product is formed and that methyl migration does not occur; all ${}^{13}C$-labeled atoms still bear a single methyl group. Three of the labeled carbon signals are assigned as quaternary sp$^2$-hybridized carbon atoms $C_2$, $C_3$ and $C_5$, based on the lack of any large ${}^1J_{CH}$ coupling constant and correlation of the chemical shift to those in the unlabeled complex. The remaining labeled carbon atom, $C_6$, has a chemical shift close to that of the unsubstituted complex and this carbon exhibits a large doublet splitting in the gated decoupled spectrum, with a ${}^1J_{CH}$ value of 127.1 Hz, indicating that a proton is directly attached to this carbon atom. Further, each ${}^{13}C$ atom also exhibits one ${}^{13}C$-${}^{13}C$ coupling ($J_{C2\text{-}C3} = 46.3$ Hz, $J_{C5\text{-}C6} = 39.3$ Hz), proof of adjacent ${}^{13}C$ atoms. One-bond $J_{CC}$ values vary widely depending on the hybridization of the two carbon atoms, much as the value of the ${}^1J_{CH}$ coupling constant depends on the carbon hybridization; furthermore, both values can be calculated.[217] The calculated values for the ${}^1J_{CC}$ coupling constant for sp$^2$-sp$^2$ and sp$^2$-sp$^3$ environments are 48.7 and 37.8 Hz, respectively, in excellent agreement with the observed values of 46.3 and 39.3 Hz. Atoms separated by larger distances have considerably smaller values; ${}^2J_{CC}$ and ${}^3J_{CC}$ values are normally less than 5 Hz. Since all available data agree that the skeletal structure of the butyne fragments remains unchanged, it is the allyl ligand that has been disrupted.

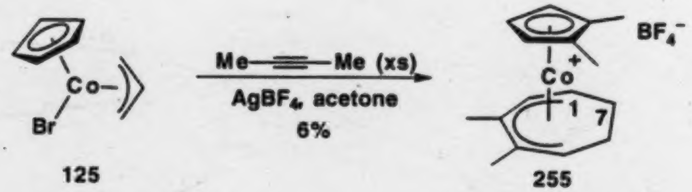


80

87-$^{13}C_4$

(Eq. 94)

The analogous reaction of $(C_5H_5)Co(\eta^3\text{-}C_3H_5)(Br)$ (**125**) with silver tetrafluoroborate and excess 2-butyne in acetone gives a complex mixture of products consisting mostly of uncharacterized paramagnetic materials, but containing small amounts of cycloheptadienyl complex **255**: a rather unexpected product (Eq. **95**). A small amount (6%) of the orange complex **255** was isolated by careful chromatographic separation. This compound is also formed in low yield by allowing the halide complex to react with 2-butyne in TFE or by allowing the triflate salt to react with excess 2-butyne in dichloromethane, although the reaction is not noticeably cleaner. The lack of a $C_5H_5$ signal in the $^1H$ NMR spectrum and appearance of several peaks in the range δ 6.0–5.4 provide some indication of the substituted cyclopentadienyl structure, but the $^1J_{CH}$ values of approximately 180 Hz for three carbon atoms in the gated decoupled $^{13}C$ NMR spectrum strongly implicate the presence of a disubstituted cyclopentadienyl ligand. The relatively large values of 180 Hz for $^1J_{CH}$ coupling constants have been noted previously in this lab and appear to be characteristic of cyclopentadienyl ligands. Correlation of these carbons to broad singlets in the $^1H$ NMR spectrum at δ 5.64, 5.33 and 5.16 is also consistent with a dimethylcyclopentadienyl structure in an unsymmetrical bonding environment.

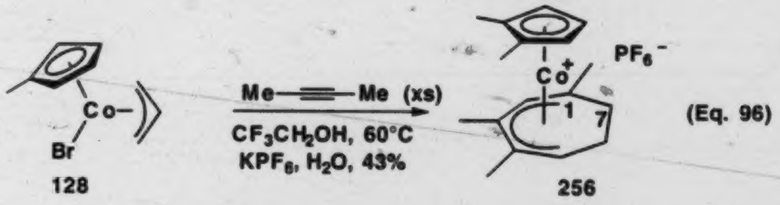


**125** **255** (Eq. 95)

After assigning these signals, the remaining resonances can be assigned as originating from a 3,4-dimethylcycloheptadienyl ligand. Characterization of the cycloheptadienyl ligand in **255** is made somewhat more difficult by overlapping signals and the complex multiplet character of several other signals in the $^1H$ NMR spectrum.

However, there is a clear doublet at δ 5.22 assigned to $H_2$, and the COSY spectrum shows this signal is correlated to a multiplet at δ 5.04, where two overlapping signals ($H_1$ and $H_5$) are observed. The four resonances for the methylene units of the cycloheptadienyl rings are observed at relatively normal (δ 2.78 ($H_{7endo}$), 1.95 ($H_{6endo}$), 1.75 ($H_{7exo}$) and 0.50 ($H_{6exo}$)) chemical shifts, although all signals are poorly resolved multiplets. The $^{13}C$ NMR spectrum, assigned with the assistance of the HMQC spectrum, proved to be of great value in assigning the complex structure. The pentadienyl fragment of the cycloheptadienyl ligand gives rise to three signals readily assigned to the methine carbons at δ 96.0 ($C_2$), 90.6 ($C_1$) and 86.2 ($C_5$). Four singlets (δ 115.5, 109.1, 102.9 and 102.6) are seen further downfield and assigned to the four quaternary $sp^2$-hybridized carbons in both cycloheptadienyl and cyclopentadienyl ligands. The methylene carbons of the seven-membered ring resonate at 38.6 ($C_7$) and 28.1 ($C_6$) ppm, respectively.

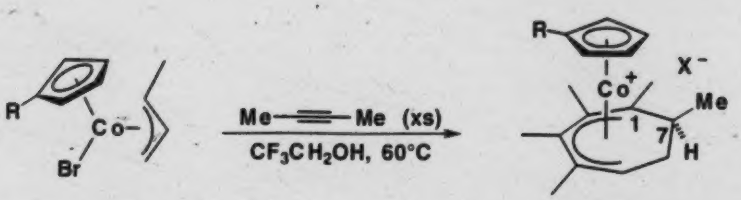
The reactivity of methylcyclopentadienyl (Cp') allyl complex **128** with butyne was also investigated; very similar chemistry is observed, although the isolated yield is more reasonable (Eq. **96**). The reaction of allyl complex **128** with excess 2-butyne in trifluoroethanol yields a moderate amount (43%) of the orange dimethylcyclopentadienyl trimethylcycloheptadienyl complex **256**. Full spectroscopic analysis was used to



(Eq. 96)

determine the structure of this dimethylcyclopentadienyl complex. Three signals at 5.29, 5.14 and 4.73 ppm in the $^1H$ NMR spectrum can be attributed to this ligand. The HMQC spectrum correlates these signals to carbon atoms at δ 88.72, 88.67 and 85.7, all of which show the characteristic value for the $^1J_{CH}$ coupling constant of 180-182 Hz. The two methyl groups are assigned to singlets at 1.89 and 1.67 ppm by their correlation to carbon signals at 10.5 and 10.3 ppm. The relatively high shielding of these methyl groups is characteristic of methyl groups on a cyclopentadienyl ligand in these cobalt complexes. This observation is similar to the shielding in $C_5Me_5$ ligands in other cationic cycloheptadienyl cobalt complexes (*vide supra*). The remaining carbon signals at 101.3 and 101.0 ppm are assigned to the quaternary $sp^2$-hybridized carbon atoms of the dimethylcyclopentadienyl ring by correlations to the ring hydrogens seen in the HMBC spectrum. A broad singlet in the $^1$H NMR spectrum at 5.14 ppm integrating to two hydrogen atoms is assigned to $H_2$ and one hydrogen atom in the dimethylcyclopentadienyl ligand, based again on the HMQC and HMBC spectra. The $H_5$ signal at $\delta$ 4.59 shows correlations to both $H_6$ protons at 2.30 and 0.90 ppm in the COSY spectrum and a second methylene unit consisting of signals at $\delta$ 2.30 ($H_{7exo}$) and 1.37 ($H_{7endo}$) completes the seven-membered ring.

In contrast to the skeletal rearrangement seen in the reactions of Cp and Cp' allyl complexes **125** and **128** with 2-butyne, the reactions of the corresponding crotyl bromide complexes **126** and **129** with excess 2-butyne yield normal cycloheptadienyl products **257** and **258** derived from a straightforward [3 + 2 + 2] cycloaddition process (Eq. **97**). It is obvious from the spectroscopic analysis that the cyclopentadienyl ligand in complex **257** remains intact, resonating as a singlet at 5.35 ppm in the $^1$H NMR spectrum and at 89.7 ppm ($^1J_{CH}$ = 182 Hz) in the $^{13}$C NMR spectrum. Four quaternary carbon signals (115.2, 106.7, 105.1 and 103.7 ppm) are attributed to the tetrasubstituted pentadienyl portion of the molecule. The remaining carbon ($C_5$) resonates at $\delta$ 81.7 and correlates to a multiplet at $\delta$ 5.35 ($H_5$) in the $^1$H NMR spectrum. Three other signals ($\delta$ 2.72, 2.57 and 0.99) are assigned to $H_{6endo}$, $H_7$ and $H_{6exo}$, respectively. Interestingly, the *endo* methyl group on the $C_7$ carbon is somewhat shielded and resonates at $\delta$ 0.38 in the $^1$H NMR spectrum; although, in the $^{13}$C spectrum, the carbon ($\delta$ 20.4) appears to be only slightly affected. While it is indeed bewildering that this slight change from allyl to crotyl could cause such a dramatic change in reactivity pattern, this observation will be discussed shortly.



(Eq. 97)

R = H (126)
R = Me (129)

257, R = H, X = Br (54%)
258, R = Me, X = $PF_6$ (39%)

Comparison of the $^1$H NMR data (Table 6) for the 2-butyne allyl/alkyne cycloaddition products presented above is difficult, as the products are obtained through different mechanisms and thus have different structures. Furthermore, a good portion of the coupling constant information could not be readily obtained due to overlapping or multiplet signals. However, some trends are observable. Both Cp* templates yield products (**87** and **254**) with slightly distorted cycloheptadienyl conformations, due to the large steric bulk of both ligands and the unique presence of the *exo*-methyl substituents. This is evident in the values of coupling constants and the chemical shifts for the hydrogen atoms on $C_6$ and $C_7$. Especially noticeable is the upfield shift of $H_{6endo}$ due to the conformational perturbation of the *exo* methyl group. The reaction of 2-butyne with the $C_5H_5$ and $MeC_5H_5$ allyl complexes **125** and **128** yield $\eta^5$-cycloheptadienyl products **255** and **256**. These complexes, although containing a new dimethylcyclopentadienyl ligand, have cycloheptadienyl ligands that have spectroscopic patterns similar to previously discussed cycloheptadienyl complexes. All products from crotyl precursors (**254**, **257**, and **258**) have an *endo*-methyl group on carbon seven, which shifts the $H_{7exo}$ proton downfield from about 1.4 ppm to about 2.5 ppm.

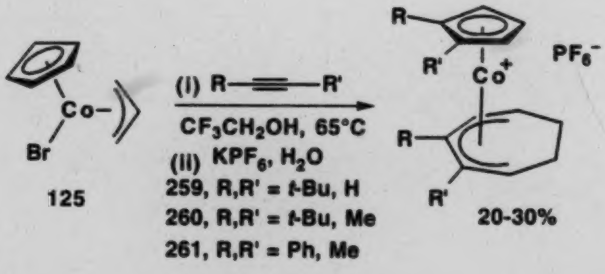
**Table 6.** Comparative $^1$H NMR Spectroscopic Data For 2-Butyne Derived $\eta^5$-Cycloheptadienyl Complexes

| | **87** | **254** | **255** | **256** | **257** | **258** |
|---|---|---|---|---|---|---|
| **$H_1$**<br>$J_{1\text{-}2}$ | 4.09 (dd)<br>b | 3.78 (d)<br>b | 5.03(m)<br>9.4 Hz | b | b | b |
| **$H_2$**<br>$J_{2\text{-}3}$ | b | b | 5.22 (d) | 5.14 (s)<br>b | b | b |
| **$H_3$**<br>$J_{3\text{-}4}$ | b | b | b | b | b | b |
| **$H_4$**<br>$J_{4\text{-}5}$ | 5.10 (s)<br>b | 4.91 (s)<br>b | b | b | b | b |
| **$H_5$**<br>$J_{5\text{-}6endo}$<br>$J_{5\text{-}6exo}$ | b | b | 5.03 (m)<br>a<br>a | 4.59 (dd)<br>6.6 Hz<br>4.0 Hz | 5.35 (m)<br>5.8 Hz<br>3.6 Hz | 5.08 (dd)<br>5.4 Hz<br>3.6 Hz |
| **$H_{6endo}$**<br>$J_{6endo\text{-}6exo}$<br>$J_{6endo\text{-}7endo}$<br>$J_{6endo\text{-}7exo}$ | 0.75 (m)<br>b<br>9.5 Hz<br>4.5 Hz | -0.12 (dq)<br>b<br>b<br>10.0 Hz | 1.95 (m)<br>a<br>a<br>a | 2.3 (m)<br>14.3 Hz<br>a<br>a | 2.72 (ddd)<br>15.2 Hz<br>b<br>9.1 Hz | 2.84 (ddd)<br>15.3 Hz<br>b<br>9.3 Hz |
| **$H_{6exo}$**<br>$J_{6exo\text{-}7endo}$<br>$J_{6exo\text{-}7exo}$ | b | b | 0.50 (m)<br>a<br>a | 0.92 (m)<br>6.4 Hz<br>6.4 Hz | 0.99 (ddd)<br>b<br>3.6 Hz | 1.14 (ddd)<br>b<br>3.9 Hz |
| **$H_{7endo}$**<br>$J_{7endo\text{-}7exo}$<br>$J_{7endo\text{-}1}$ | 2.39 (ddd)<br>15.7 Hz<br>4 Hz | b | 2.75 (m)<br>16 Hz<br>a | 2.3 (m)<br>15.1 Hz<br>b | b | b |
| **$H_{7exo}$**<br>$J_{7exo\text{-}1}$ | 1.88 (m)<br>4 Hz | 2.56 (dqd)<br>3.1 H | 1.75 (m)<br>a | 1.37 (d)<br>b | 2.57 (m)<br>b | 2.55 (m)<br>b |

[a] Numerical value for the coupling constant was not obtained due to second order character or complexity of the signal. [b] Not applicable due to a non- hydrogen substituent.

### *B. Other Anomalous [3 + 2 + 2] Cycloaddition Reactions*

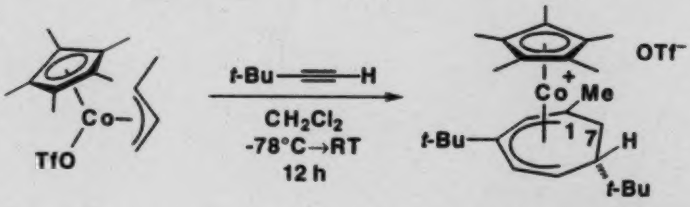
Further exploration of the alkyne cycloaddition chemistry of $(C_5H_5)Co(\eta^3\text{-}C_3H_5)(Br)$ **125** reveals that this astonishing rearrangement is relatively common. In addition to 2-butyne, the reactions of **125** with 1-phenylpropyne, *t*-butylacetylene and 4,4-dimethyl-2-pentyne all appear to form dialkylcyclopentadienyl products **259-261** upon treatment in TFE at 65°C (Eq. **98**). These cycloheptadienyl salts are reasonably water soluble, whereas many of the impurities are not. Crude separation was thus effected by a simple aqueous extraction, followed by precipitation of the cobalt cation with $KPF_6$. The insoluble hexafluorophosphate salt is either directly collected by filtration, or extracted into $CH_2Cl_2$, to give purified products **259-261** in isolated yields of 15-20%. Because these products are not formed in high yield, characterization of new compounds is provided by $^1H$ NMR and electrospray mass spectrometry only, both of which are fully consistent with the suggested structures. Initial studies suggest that the analogous reactions of methylcyclopentadienyl complex **128** with these alkynes also undergo this rearrangement.



(Eq. 98)

Allowing the cobalt allyl complex **125** to react with acetylene-$d_2$ and silver tetrafluoroborate gives a tetradeuterated cycloheptadienyl product that does not show any significant deuterium incorporation into the $C_5H_5$ ring, similar to **99-d₄**, obtained from the reaction of Cp* allyl triflate complex **80** with acetylene-$d_2$. It must be concluded that, at least with acetylene, the normal [3 + 2 + 2] cycloaddition pathway is in effect. Only with larger alkyne substituents does the reactivity pathway become "abnormal".

In addition to the product obtained from the reaction of crotyl triflate complex **81** with 2-butyne, one other alkyne gives an anomalous cycloheptadienyl complex. When crotyl triflate complex **81** reacts with an excess of *t*-butylacetylene in $CH_2Cl_2$, an inseparable 2:1 mixture of products is obtained, along with traces of unidentified material. The major product is tentatively assigned by $^1H$ NMR spectroscopy to be the $\eta^5$-cycloheptadienyl complex **262** (Eq. **99**). The minor product appears to be a seven-membered ring as well, but too many signals are obscured to conclusively determine the structure. Characteristic features of the major complex are the appearance of a singlet ($\delta$ 4.63, $H_2$), a doublet ($\delta$ 5.09, J = 8.2 Hz, $H_4$) and a doublet of doublets ($\delta$ 4.01, J = 8.0, 5.3 Hz, $H_5$) in the $^1H$ NMR spectrum. The $H_{6endo}$ proton (-0.16 ppm) is significantly shielded and the $C_7$ protons ($\delta$ 2.52 and 2.00) are also somewhat perturbed. The methyl group is not attached to a sp$^3$ carbon on the ring, as a characteristic methyl doublet is absent in the $^1H$ NMR spectrum. The substitution pattern suggests that the integrity of the crotyl ligand is not maintained and that a rearrangement has occurred related to but not identical to that seen in complex **87**, the product of the reaction between **81** and 2-butyne.



(Eq. 99)

**81**

**262, major isomer**

### *C. Mechanistic Proposals*

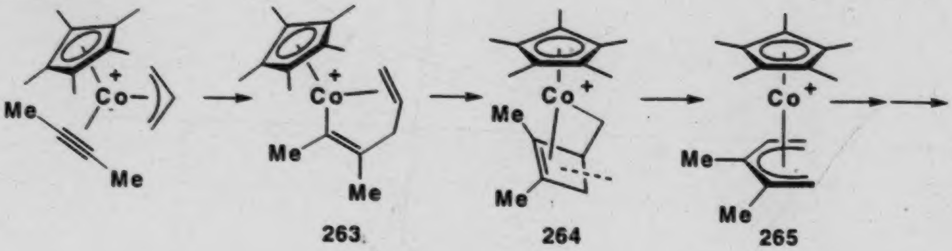
The substitution pattern of the cycloheptadienyl product **87** obtained when pentamethylcyclopentadienyl cobalt allyl complex **80** reacts with doubly $^{13}$C-labeled 2-butyne indicates that the allyl ligand likely undergoes carbon-carbon bond cleavage and rearrangement at some point in the process, while the 2-butyne portions remain intact throughout the reaction. Mechanistically, there are several related proposals that each accomplish this transformation, all involving rearrangements that occur after the insertion of the allyl into the first coordinated alkyne.

The reactions of the cyclopentadienyl and methylcyclopentadienyl templates with 2-butyne give an important mechanistic clue; in order to form a dimethylcyclopentadienyl product, a [3 + 2] cycloaddition must be a critical step in the mechanistic process. This indicates that the original cyclopentadienyl ligand reacts to form the seven-membered ring; the allyl ligand is incorporated into the new dimethylcyclopentadienyl ligand. Some of these proposals, although possibilities for the $C_5Me_5$ template, are inconsistent with the formation of the dimethylcyclopentadienyl products.

#### *1. $\eta^5$-Pentadienyl Intermediates*

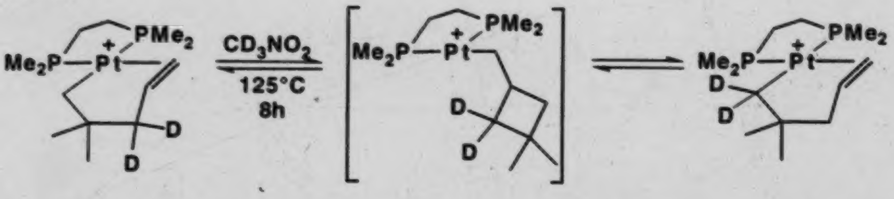
One possible mechanism to accomplish the observed rearrangement involves cyclization and ring opening of vinyl olefin intermediate **263** to a cyclobutenyl intermediate (Scheme **46**). The initial steps of coordination and insertion of the alkyne to form **263** are identical to those proposed for the [3 + 2 + 2] pathway. However, ring closure from the vinyl olefin to a four-membered ring can then conceivably occur, generating (cyclobutenyl)methyl complex **264** which can subsequently undergo carbon-carbon bond activation of the other β-carbon-carbon bond to form the σ-alkyl π-diene ($\eta^5$-pentadienyl) complex **265**.

**Scheme 46**



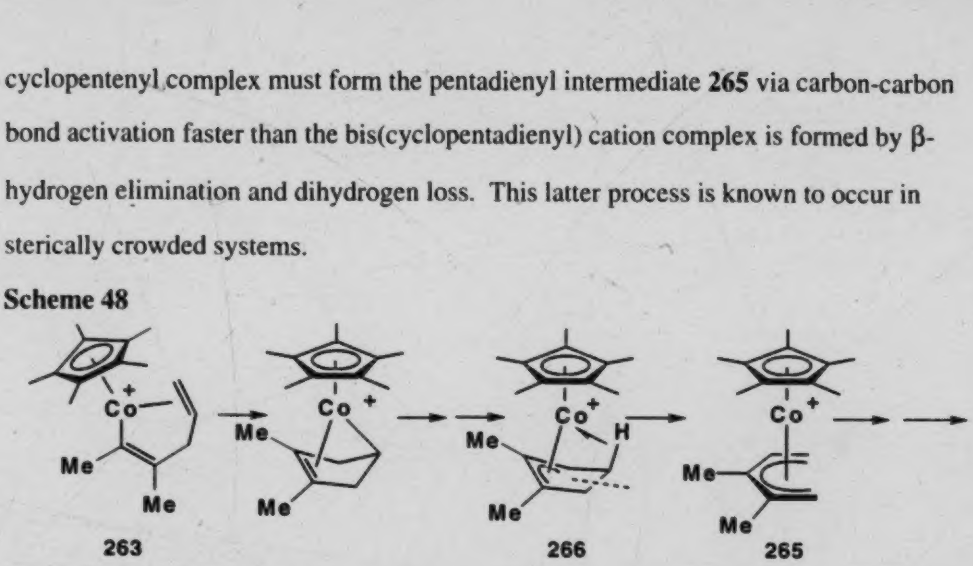
Although many of these intermediates are formally unsaturated 16 electron complexes, it is likely that stabilization is effected by coordination of solvent or the triflate counterion. A similar process, the reversible closure to a four-membered cyclobutane ring, which has a ring strain energy of about 28 kcal/mol, has been observed in Flood's platinum systems (Scheme **47**).[153c] Subsequent alkyne insertion into intermediate **265**, although not a precedented reaction process, would complete the seven-membered ring formation.

**Scheme 47**



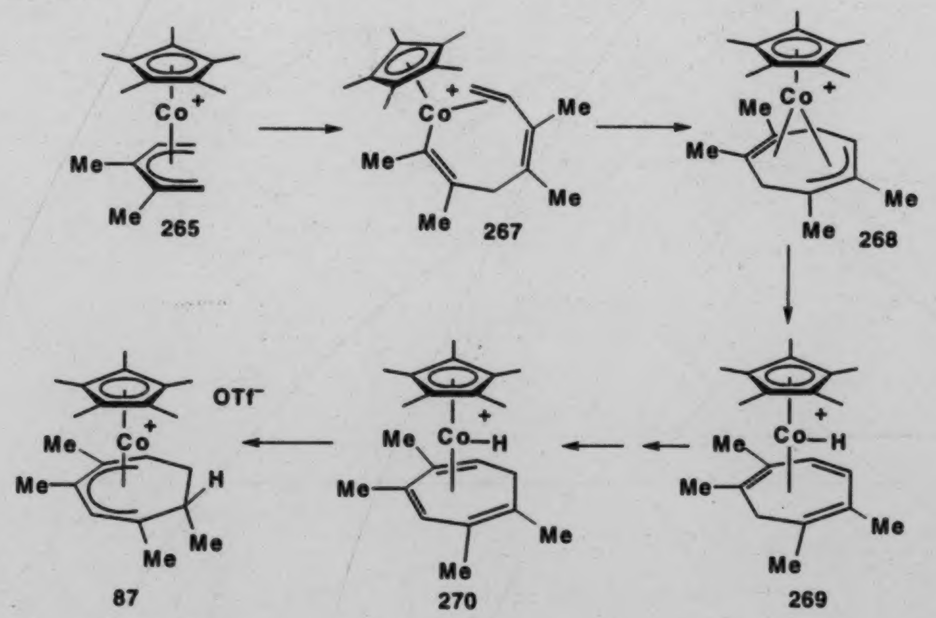
Another possible route to $\eta^5$-pentadienyl intermediate **265** is illustrated in Scheme **48**. Rather than undergoing a migratory insertion to form a four-membered ring, the vinyl ligand can migrate to the terminal carbon of the olefin, forming an $\eta^1,\eta^2$-cyclopentenyl intermediate. This process has been proposed in the synthesis of cyclopentadienyl ligands from [3 + 2] allyl/alkyne cycloaddition reactions.[61,62,83-86,88,120] β-Hydride elimination and hydride reinsertion from this $\eta^1,\eta^2$-cyclopentenyl intermediate create a new $\eta^3$-cyclopentenyl (**266**). Although this cyclization process is well known, facile dehydrogenation generally occurs to form a cationic cyclopentadienyl complex.[61,62,83-86,88,120] In order to produce the cycloheptadienyl complexes, this cyclopentenyl complex must form the pentadienyl intermediate **265** via carbon-carbon bond activation faster than the bis(cyclopentadienyl) cation complex is formed by β-hydrogen elimination and dihydrogen loss. This latter process is known to occur in sterically crowded systems.

**Scheme 48**


Co+
Me
Me
263
Co +
Me
Me
Co+
H
Me
Me
266
Co+
Me
Me
265

However intermediate **265** may form, insertion of another equivalent of alkyne into **265** would produce a vinyl diene complex **267**, an intermediate rearranged from that proposed to form in the normal [3 + 2 + 2] cycloaddition reactions (Scheme **49**).

**Scheme 49**


Co+
Me
Me
265
Co+
Me
Me
Me
Me
267
Co +
Me
Me
Me
Me
268
OTf⁻
Co+
Me
Me
H
Me
Me
87
Co—H
+
Me
Me
Me
Me
270
Co—H
+
Me
Me
Me
Me
269

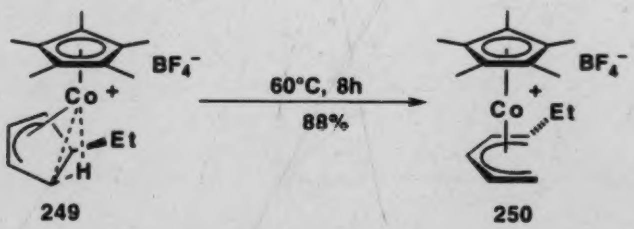
Cyclization of this vinyl diene complex would give a tetramethylcycloheptadienyl complex **268** that has the complete carbon skeleton of the final product. Intermediate **268** is an allyl-olefin complex, and repeated β-hydride elimination reactions can form triene hydride **270**. From this intermediate, hydride migration provides the final $\eta^5$-cycloheptadienyl complex **87**.

The triene hydride intermediate **270** common to both of these routes presumably goes through a series of $\eta^1,\eta^4$-σ-diene intermediates before the final irreversible hydride insertion to form the observed $\eta^5$ isomer, as described for the [3 + 2 + 2] cycloaddition reactions (Chapter 2). However, this mechanism does not satisfactorily rationalize the formation of one specific regiochemistry in the final product from a plethora of possible structures. A large number of β-hydride elimination processes are apparent in Schwiebert's iridium system, where, in some cases, several cycloheptadienyl isomers are formed.[60,61] The lack of multiple products in this cobalt manifold suggests other pathways are in effect.

The above rationalization accommodates the formation of the observed ($\eta^5$-$C_5Me_5$)Co($\eta^5$-cycloheptadienyl) products **87** and **254** but it seems unlikely that the coordinatively saturated $\eta^5$-pentadienyl intermediate **265** would react further with an alkyne. To evaluate the reactivity of such a coordinatively saturated $\eta^5$-pentadienyl complex, $\eta^5$-1-propylpentadienyl complex **252** was prepared according to the method of Spencer.[128] The reaction of ($\eta^5$-$C_5Me_5$)Co($\eta^5$-1-propylpentadienyl) complex **252** with 2-butyne in dichloromethane at room temperature or dichloroethane at 60°C yields a mixture of unidentified products, although cycloheptadienyl complexes are notably absent. The lack of an isolable $\eta^5$-cycloheptadienyl complex in this reaction suggests that the open $\eta^5$-pentadienyl structure is not a competent intermediate in the formation of seven-membered ring products. However, there remains a possibility that interaction with the alkyne is faster than rearrangement of a distorted "σ-diene" intermediate or a unsaturated $\eta^1,\eta^2$-sigma olefin intermediate to the inert planar $\eta^5$-pentadienyl structure.

The possibility of a "ring slip" of the $C_5Me_5$ ligand from $\eta^5$- to $\eta^3$-hapticity, or the analogous "slip" in the pentadienyl ligand could provide a coordination site for the alkyne. However, the most probable fate of such a complex is loss of the alkyne, and the re-establishment of the $\eta^5$-ligand.

Another serious flaw in the proposed cyclopentenyl reaction pathway (Scheme **48**), aside from the previously mentioned reactivity of the pentadienyl structure, is that the activation of the ring carbon-carbon bond is unlikely to occur under these conditions. Spencer does not observe carbon-carbon bond activation in a well characterized and very similar agostic cyclopentenyl complex until the compound is heated to 60 °C (Eq. **100**).[128] In our case, cleavage of the cyclopentenyl intermediate **249** must occur well below room temperature, incompatible with Spencer's results. Additionally, intermediate pentadienyl complexes such as **250** have never been observed in our chemistry under conditions of limited alkyne concentration, which might be expected if carbon-carbon activation of the cyclopentenyl intermediate takes place. Further, this process does not rationalize the formation of dimethylcyclopentadienyl products from the $C_5H_5$ or $C_5H_4Me$ allyl templates.



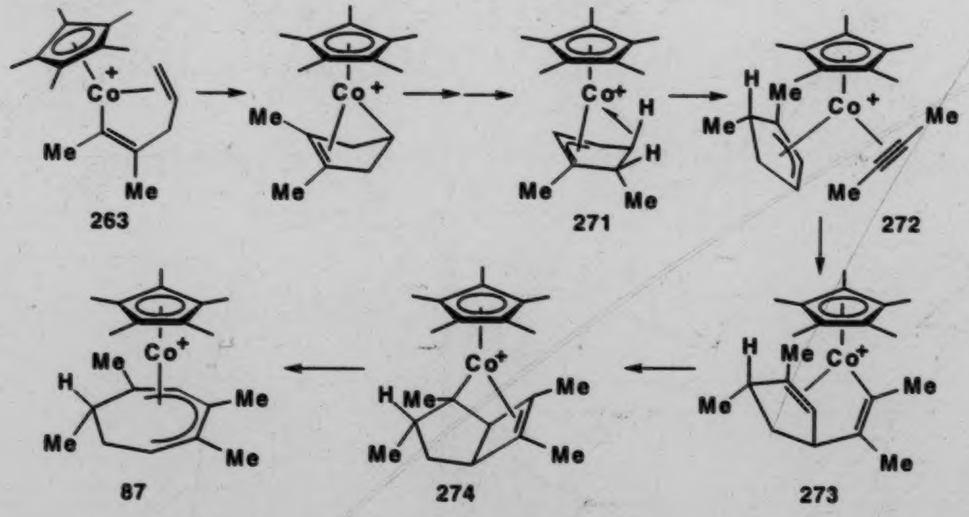
**249** **250**

(Eq. 100)

### 2. *Alkyne Insertion Into $\eta^3$-Cyclopentenyl Intermediates and Rearrangement to $\eta^5$-Cycloheptadienyl Products*

A more reasonable reaction pathway (Scheme **50**) for the formation of $\eta^5$-cycloheptadienyl complex **87** also involves formation of an $\eta^3$-cyclopentenyl ligand **271** from cyclization of vinyl olefin **263** (Scheme **50**). This proposal accomodates both the anomalous [3 + 2 + 2] cycloaddition reactions and the cyclopentadienyl "exchange" results observed for the reactions of the $C_5H_5$ and $C_5H_4Me$ allyl templates. Similar to Spencer's chemistry, we propose the formation of the thermodynamically most stable $\eta^3$-cyclopentenyl structure (**271**) from the initial cyclization product, placing the hydride down onto the substituted carbon to relieve the "cis-butene" like torsional strain. This endocyclic allyl (cyclopentenyl) complex **271** then coordinates a second alkyne to form allyl alkyne intermediate **272**. In this view, the β-H elimination/re-insertion process is simply trapped by alkyne coordination at the most stable intermediate. From here, several alternatives can be invoked to rationalize the formation of the observed product. In one scenario, migratory insertion of the cyclopentenyl complex onto the alkyne generates the key vinylcyclopentene intermediate **273**. Migration of the vinyl ligand to the coordinated olefin then generates the strained bicyclic alkyl complex **274**. Metal-mediated non-concerted [2 + 2] ring opening forms the $\eta^5$-cycloheptadienyl product **87**.

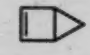
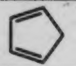
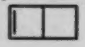
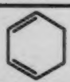
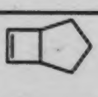
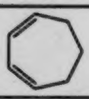
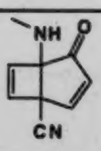
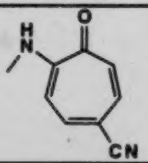
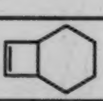
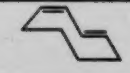
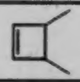
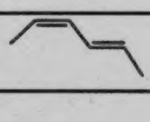
**Scheme 50**



Electrocyclic ring opening of cyclobutenes is well known to occur thermally at elevated temperatures.[218] The thermally allowed concerted process for ring opening of cyclobutene systems is required by the Woodward-Hoffmann rules to be conrotatory.

However, the "forbidden" disrotatory process can occur at substantially higher activation energy, estimated to be 15 kcal/mol less favorable than the conrotatory ring opening.[218] However, in small strained bicyclic ring systems, the conrotatory process cannot occur, as this would form a *trans* double bond, which cannot be accommodated in small (<8 membered) ring systems. However, such strained systems do undergo ring opening processes at elevated temperatures, as seen by the data in Table **7**.[218] Thermal ring opening of bicyclo[3.2.0]heptene itself occurs at 400-500°C (Entry **3**), although strong substituent effects have been observed, dramatically enhancing the rates and changing the mechanism for ring opening in both amino- and cyano-substituted bicyclo[3.2.0]heptene compounds (*i.e.*, Entry **4**). Rather than a concerted electrocyclic process that is seen in unconstrained systems, small ring systems can undergo ring opening via a diradical pathway. The amino- and cyano- substituents help stabilize the radical intermediate, thus lowering the activation energy for ring opening.

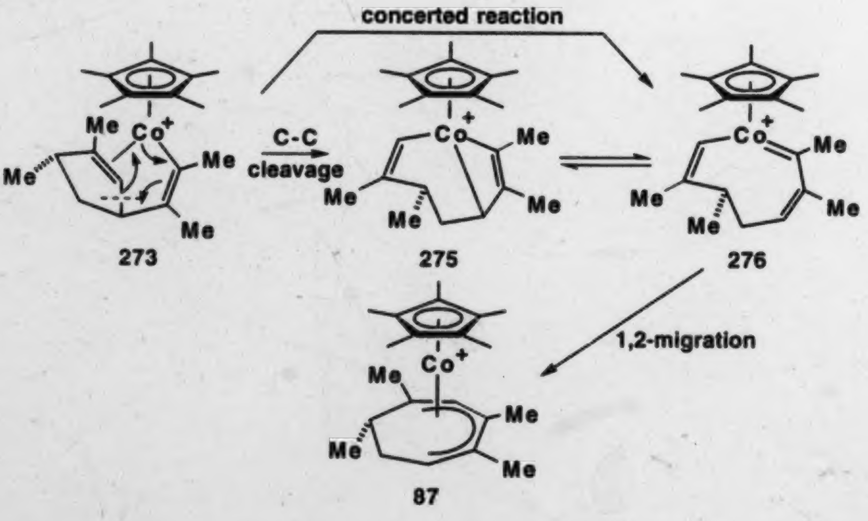
**Table 7**. Thermolysis Products of Strained Bicyclic Hydrocarbon Systems[218]

| Entry | Starting Diene | Temp (°C) | Product |
|---|---|---|---|
| **1** |  | 20-25 |  |
| **2** |  | > 150 |  |
| **3** |  | ≈ 400 |  |
| **4** |  | -75 |  |
| **5** |  | 250 |  |
| **6** |  | 175-180 |  |

Assuming that the cobalt bonding stabilizes radical-like intermediates, ring opening of cobalt intermediate **274** may thus be observed at relatively low temperatures. Other metal catalyzed ring opening reactions occur by both formally allowed and disallowed pathways.[219a,b] In particular, the metal-mediated ring opening reaction of a bicyclo[3.2.0]heptene system and gas phase reactions of $CpFe^+$ with alkynes are reported to proceed via a similar pathway.[219c,d]

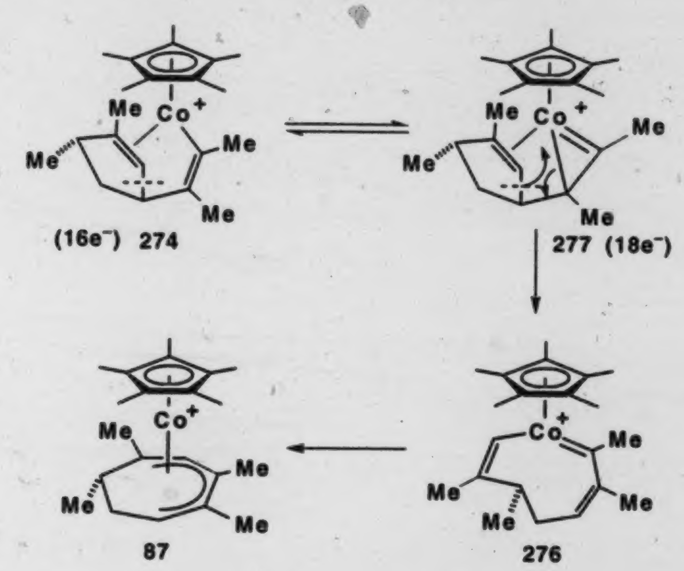
The ring strain in cyclobutene itself is 28.5 kcal/mol[218] and although this does not necessarily rule out the formation of cyclobutene intermediate **274**, other possible mechanisms avoid the formation of such a high-energy intermediate. The vinyl cyclopentene intermediate complex **273** could alternatively undergo direct carbon-carbon bond activation of the cyclopentene ring adjacent to the coordinated olefin (Scheme **51**). This generates what appears to be a bicyclic Co(V) intermediate (**275**); however, this structure can relax into a Co(III) vinyl carbene structure (**276**). 1,2-Migration of the metal vinyl to the carbene, a well-precedented fundamental reaction,[220] closes the carbocyclic ring to form the $\eta^5$-cycloheptadienyl product.

**Scheme 51**



An $\eta^2$-vinyl structure (**277**) related to **273** can be used to view this process from another perspective: a "simple" β-carbon elimination (Scheme **52**). In this 1-metallacyclopropene structure, a β-carbon elimination reaction forms intermediate **276** directly. Casey has described several examples of isolable or intermediate 1-metallacyclopropene complexes from the protonation of alkyne complexes.[221]

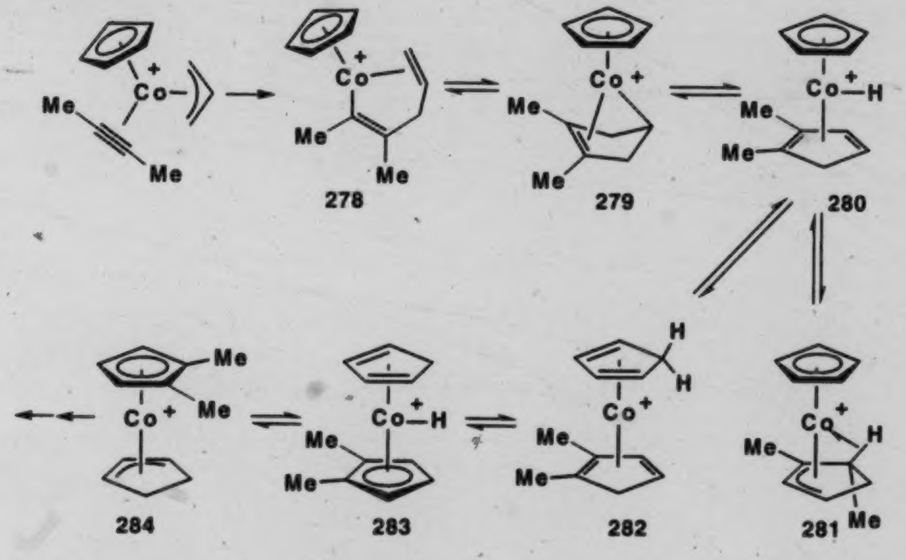
**Scheme 52**.



Both of these proposals (Schemes **51** and **52**) have several advantages over the previously proposed mechanisms. Only one cycloheptadienyl product is formed, via processes that offer little possibility for other isomers. Only a few assumptions are made in this proposal. The $\eta^3$-cyclopentenyl intermediate that reacts with the alkyne must be the isomer with one methyl group on an $sp^3$-carbon (**271**). It also is assumed that the insertion of the alkyne into the cyclopentenyl ligand occurs at the less substituted side of the cyclopentenyl ligand. This mechanism demands that β-hydride elimination and hydride insertions are fast relative to the coordination of a second alkyne. This does not preclude the possibility that an agostic cyclopentenyl complex, similar to Spencer's isolable ethylcyclopentenyl, forms and equilibrates rapidly via hydridocobalt diene intermediates. In this case, the cyclopentenyl intermediate **271** then preferentially reacts with the alkyne, draining the equilibrium toward a single product. This proposal fits the $^{13}$C labeling results from the reaction of **87** with doubly $^{13}$C-labeled 2-butyne.

In the allyl templates **125** and **128**, the observation of the cyclopentadienyl ligand "exchange" is also accommodated by these mechanistic proposals. The formation of σ-π intermediate **279** is the result of the cyclization of vinyl olefin intermediate **278** (Scheme **53**). The nonconjugated cyclopentenyl intermediate **279** then undergoes β-hydrogen

**Scheme 53**

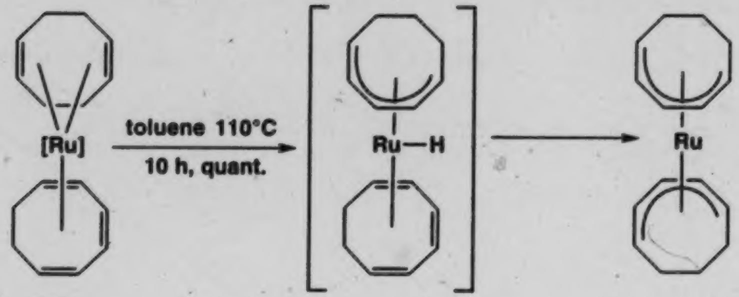


elimination to give diene hydride **280**, which may be in equilibrium with the agostic structure **281**. Although the ring opening pathway proposed above for the $C_5Me_5$ systems may exist, other pathways may dominate in less hindered systems. Migration of the hydride ligand can occur back to the dimethylcyclopentadiene ligand, but the hydride may also migrate to the η$^5$-cyclopentadienyl ring (a formal reductive elimination), forming the pseudo-symmetrical bis(diene) intermediate **282**. Activation of the carbon-hydrogen bond of the dimethylcyclopentadiene (an oxidative addition reaction) reforms a cobalt(III) diene hydride **283**, with the cyclopentadiene and cyclopentadienyl rings now inverted. Subsequent hydride insertion into the diene creates a new endocyclic η$^3$-

cyclopentenyl fragment **284**. Further reaction with alkyne occurs to form the observed dimethylcycloheptadienyl product **255**, as discussed above.

In order to produce a single product, one of two phenomena must occur. In one case, all of the proposed hydride eliminations and re-insertions are in equilibrium, driven to products by the greater stability of the dimethylcyclopentadienyl ligand compared to the unsubstituted cyclopentadienyl. Alternatively, the rate of alkyne insertion to **284** must be much faster than the rate of insertion to **281**, draining off an unfavorable equilibrium by this kinetic partitioning. Even the methylcyclopentadienyl allyl complex **128** (Eq. **94**, page 153) apparently undergoes this rearrangement, favoring a dimethylcyclopentadienyl complex exclusively over the methylcyclopentadienyl complex. Again, these hydride shifts must be fast compared to coordination of the second alkyne in order for these rearranged intermediates to form.

The migration of the hydride ligand from one ring to the other is not unreasonable, as related transfers have been observed in ruthenium chemistry (Eq. **101**). Thermolysis of **285**, for example, yields bis($\eta^5$-cyclooctadienyl) ruthenium. Isomerization of **285** to a 1,3-cyclooctadiene complex is followed by allylic carbon-hydrogen activation, and transfer of the hydride to the 1,3,5-cyclooctatriene ligand.[222]

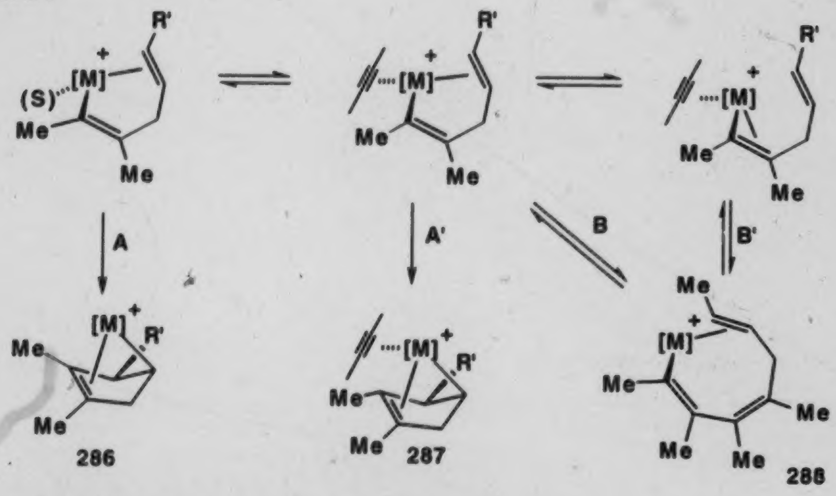


**285**

(Eq. 101)

To rationalize why some reactions appear to follow a [3 + 2 + 2] allyl/alkyne cycloaddition pathway, while others undergo a [5 + 2] ring opening process, consider the relative rates of ring closure (Path **A**) versus alkyne insertion (Path **B**) in the vinyl olefin intermediate (Scheme **54**). In $C_5Me_5$ allyl and crotyl complexes, the large steric presence of the pentamethylcyclopentadienyl ligand hinders coordination of the second alkyne. The relatively strongly electron donating $C_5Me_5$ ligand may also stabilize $16e^-$ intermediates, thus allowing time for the vinyl olefin to cyclize and rearrange to cyclopentenyl **286** (Path **A**). With Cp and Cp' allyl complexes **126** and **129**, there is both

**Scheme 54**

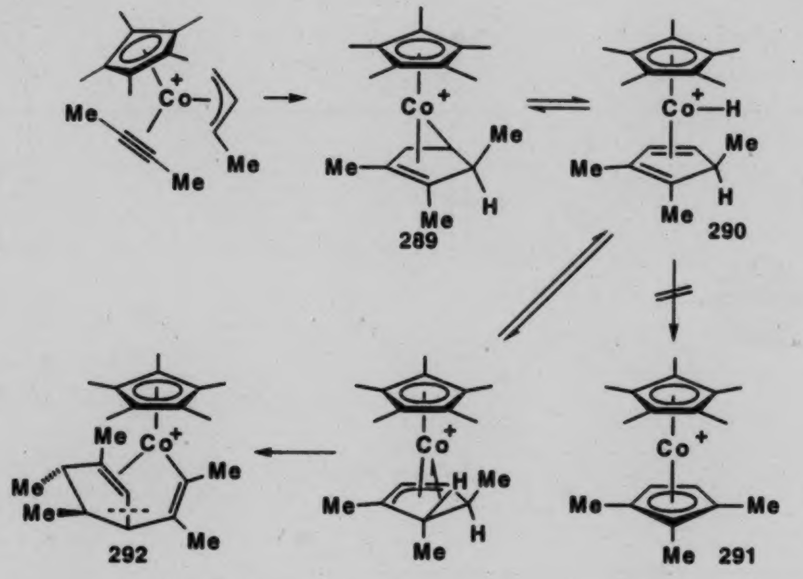


[M] = $(C_5Me_5)Co$ or $(C_5H_5)Co$ or $(MeC_5H_4)Co$
S = solvent

a lower electron density at cobalt and less steric interaction between the ligands and approaching alkyne. Although the alkyne may coordinate to help stabilize the more electron poor cobalt, cyclization to five-membered ring **287** may occur preferentially over alkyne insertion (Scheme **54**, Path **A'**). This process ultimately forms the new dimethylcyclopentadienyl ligand. The preferential cyclization may reflect a lower steric barrier to migration of the vinyl ligand to the unsubstituted coordinated olefin and a higher insertion barrier to the disubstituted alkyne. However, with crotyl complexes, the extra methyl group on the pendant olefin may inhibit vinyl migration and thus the rate of ring closure, resulting in consecutive alkyne insertions to form vinyl intermediate **288** (Path **B**). An opposite view is that the terminal olefin on the chain does not coordinate at all to the metal (Path **B'**). In this scenario, the cobalt center is highly unsaturated; thus, the vinyl group or alkyne may act as a four electron donor to help stabilize the metal center. Competitive $\eta^1,\eta^2$-vinyl coordination may explain why the terminal olefin dissociates from the metal center. Coordination of the second alkyne is therefore fast relative to olefin recoordination and ring closure, resulting in the formation of the [3 + 2 + 2] cycloaddition product.

Since we have shown that Cp*Co crotyl complex **81** inserts two acetylene molecules to form a cycloheptadienyl product with an *endo*-methyl stereochemistry (Chapter 2, page 56) the intermediates **289** and **290** (Scheme **55**) presumably have *endo* methyl groups as well. A high barrier therefore exists to dehydrogenative aromatization

**Scheme 55**

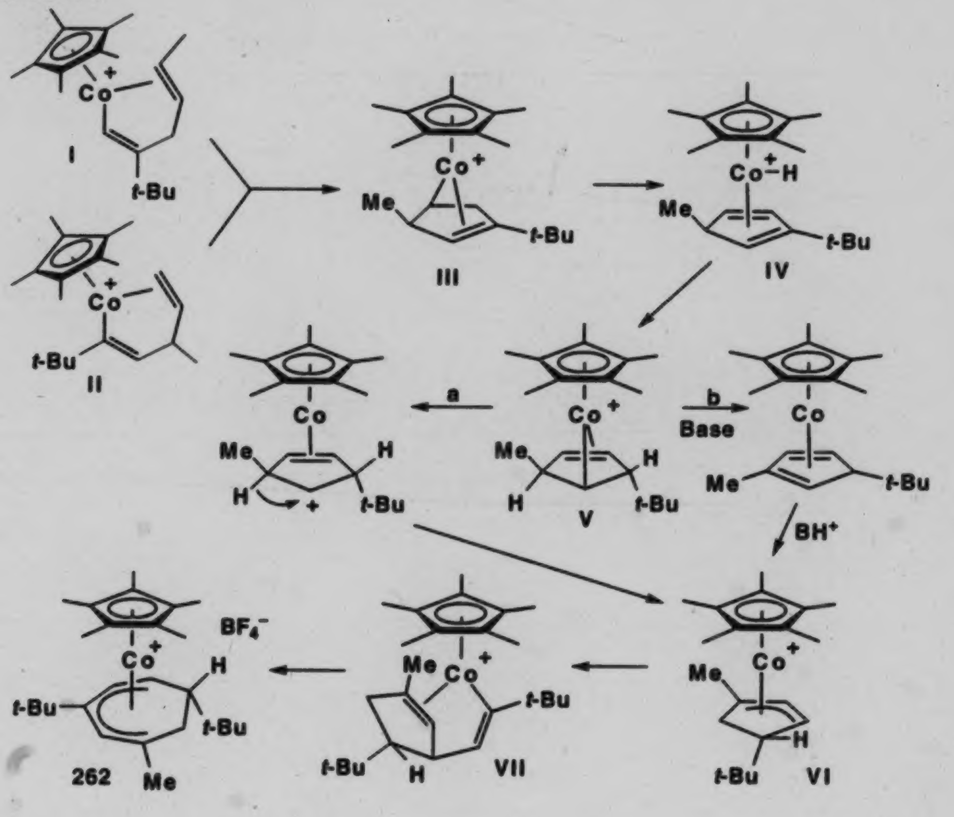


leading to a trimethylcyclopentadienyl complex **291**. In order to form an aromatic cyclopentadienyl ring (**291**), either an *exo* [1,5]-hydride shift or carbon-carbon activation of the *endo* methyl group must occur from **290**, both of which presumably have relatively high energy barriers. Another potential mechanism involves the deprotonation of the cyclopentenyl ligand by an external base and subsequent re-protonation at the metal.

This acid-base reaction pattern likely occurs in related ruthenium chemistry from this group.[120] Intermediate **292**, formed from alkyne insertion into the cyclopentenyl intermediate, presumably forms the cycloheptadienyl product **254** via further reactions, as discussed above.

The rearrangement that takes place to form complex **262** (Eq. **99**, page 160) can now be more easily explained, although the assignment of this complex is still tentative. The following mechanistic rationale also contains steps that are unique to this particular complex and, as such, is relatively more speculative. Starting from the crotyl triflate complex **81**, coordination and insertion of *t*-butylacetylene forms vinyl olefin intermediate **I** or **II** (Scheme **56**). Note that the product **262** does not allow a distinction

**Scheme 56**


Co+
I
t-Bu
Co+
t-Bu
II
Co+
Me
t-Bu
III
Co+-H
Me
t-Bu
IV
Co
Me
H
H
+
t-Bu
a
Co+
Me
H
H
V
t-Bu
b
Base
Co
Me
t-Bu
BH+
BF4-
Co+
H
t-Bu
t-Bu
262
Me
Me
Co+
t-Bu
t-Bu
H
VII
Co+
Me
H
t-Bu
VI

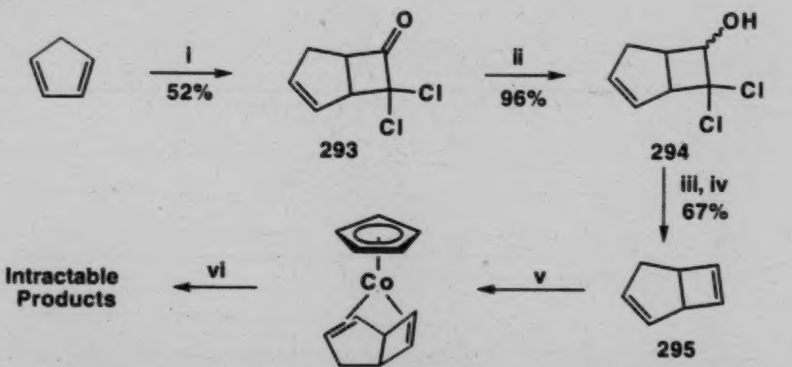
to be made between insertion structures **I** and **II**. All other insertion modes lead to products with adjacent alkyl groups, which is a stereochemistry not observed in the major product in this reaction. Cyclization to a five-membered ring (**III**) occurs, followed by a series of hydride rearrangements to form cyclopentenyl intermediate **V**. Note that β-hydride elimination and reinsertion reactions are not sufficient to form **VI**, but a hydride shift must also occur to move the methyl group from the *endo* position. Consistent with the σ-diene intermediates proposed in both ruthenium and cobalt cycloheptadienyl formation, the initial β-hydride elimination product **IV** may reinsert to form a σ–π intermediate **V**.

This is apparently an exception to the other rearrangements of cobalt cyclopentenyl intermediates to reinsert directly on top of an alkyl group, and reflects a strong tendency to place the bulky *t*-butyl group away from the metal center. It is possible that the σ-bound carbon atom in intermediate **V** has sufficient carbocation character that a [1,2]-hydride shift occurs (Path **A**), directly forming the "active" cyclopentenyl complex **VI**. Another possibility is an external base deprotonating an *exo* hydrogen in intermediate **V** (Path **B**) and then protonating the metal center. As previously mentioned, this base-mediated hydrogen atom shuttle has been implicated in ruthenium-based chemistry in this group.[120] Insertion of the second alkyne into the less substituted end of the cyclopentenyl ligand forms vinyl olefin **VII**, which converts to the observed product **262**.

### *D. Attempted Synthesis and Reactivity of a Proposed Intermediate*

Several of the proposed intermediates in the reaction mechanism may be accessible by independent synthesis, permitting an assessment of the competency of the proposed mechanism. Bicyclo[3.2.0]heptadiene **295**[223] is readily synthesized from cyclopentadiene (Scheme **57**) and, upon coordination to cobalt, protonation may provide an intermediate similar to **274** in Scheme **50**. Cyclopentadiene undergoes a thermal [2 + 2] cycloaddition reaction with dichloroketene, prepared from *in situ* dehydrohalogenation

**Scheme 57**

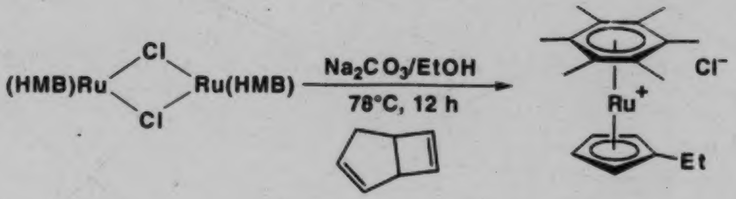


Reaction conditions: i) $Et_3N$, $Cl_2CHCOCl$, hexanes. ii) $NaBH_4$, methanol. iii) MsCl, $Et_3N$. iv) $Na/NH_3$. v) $CpCo(C_2H_4)_2$, pentane, RT, 4h. vi) $HBF_4$, alkyne, $CH_2Cl_2$.

of dichloroacetyl chloride, to yield **293**. Reduction of the bicyclic ketone gives the alcohol **294** as a 8:1 mixture of *endo* and *exo* isomers. The reaction of the resulting isomeric alcohols with methanesulfonyl chloride yields the mesylate, which is used directly in the next step without purification or characterization. Sodium reduction of the mesylate forms the diene product (**295**).

Olefin exchange of **295** with $CpCo(C_2H_4)_2$ was attempted, but does not proceed smoothly. Although the major product is tentatively assigned as the coordinated diene, the $^1H$ NMR spectrum contains several other unidentified complexes. Protonation of the exchange mixture gives only an uncharacterized mixture of paramagnetic material.

Different results are obtained when this diene reacts with other transition metal complexes. Sodium carbonate reduction of $[(C_6Me_6)RuCl_2]_2$ in ethanol in the presence of bicyclo[3.2.0]heptadiene gives $[(C_6Me_6)Ru(1\text{-}Et\text{-}C_5H_4)]^+ Cl^-$ as the only identifiable organometallic product, in good (70%) yield (Eq. **102**). Similar reduction of $[(C_5Me_5)IrCl_2]_2$ also produces an ethylcyclopentadienyl complex, but in low yield.



(Eq. 102)

The failure to synthesize the proposed bicyclic intermediate is somewhat discouraging. We thus decided to target intermediates further back along the proposed mechanistic pathway. Unfortunately, this does not allow us to distinguish between several of the key intermediates, but still allows a test of the overall mechanistic proposal that the reaction proceeds via kinetic formation and cleavage of an unsaturated cyclopentenyl intermediate. This work has led to a new general procedure for the two carbon ring expansion of cyclopentadiene ligands, forming cycloheptadienyl ligands in high yield.

# Chapter 5. [5 + 2] Cycloaddition Reactions of Coordinated Cyclopentadiene Ligands: A New Ring Expansion Strategy for the Synthesis of $\eta^5$-Cycloheptadienyl Complexes

## I. Introduction

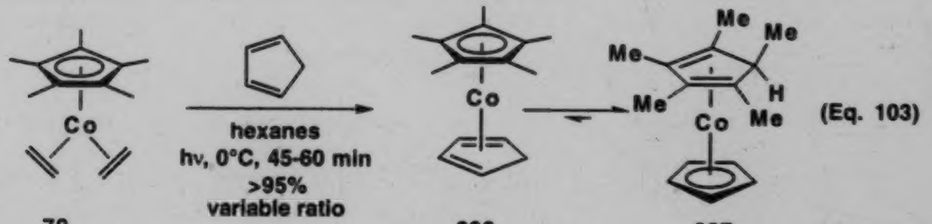
Another entry point into the proposed ring expansion mechanism involves the independent synthesis of ($\eta^5$-$C_5R_nH_{5-n}$)Co($\eta^4$-cyclopentadiene) complexes, followed by protonation of the coordinated diene to generate an $\eta^3$-cyclopentenyl ligand analogous to **271** or **284**, the proposed intermediates. This was accomplished and has led to the development of a general new ring expansion reaction in which a five-membered ring is cleaved, one alkyne molecule is inserted, and the ring is reclosed to form a coordinated seven-membered ring complex. Thus, not only have we established the competency of such an intermediate in the abnormal [3 + 2 + 2] reaction, but we have also created an entirely novel reaction of potential synthetic importance, based on an electrophilic metal-mediated carbon-carbon bond activation reaction.

## II. Results and Discussion

### A. *Preparation of Cp*Co(Cyclopentadiene) Templates*

The synthesis of ($\eta^5$-pentamethylcyclopentadienyl)cobalt($\eta^4$-cyclopentadiene) complexes is not straightforward. When attempted, thermal diene exchange with ($\eta^5$-$C_5Me_5$)Co($C_2H_4$)$_2$ **79** in hexanes at 65 °C led only to the formation of intractable material. This is likely due to cyclopentadiene dimerization at the temperatures required to initiate ethylene loss from the starting complex. Labilization of the ethylene ligand then occurs in the absence of a suitable ligand and the complex decomposes.

Photochemical exchange was then attempted using $(C_5Me_5)Co(C_2H_4)_2$ and excess cyclopentadiene, resulting in a mixture of products. Closer examination of this product mixture, however, revealed that only two compounds, ($\eta^5$-pentamethylcyclopentadienyl)cobalt($\eta^4$-cyclopentadiene) (**296**) and ($\eta^5$-cyclopentadienyl)cobalt($\eta^4$-pentamethylcyclopentadiene) (**297**) are formed (Eq. **103**). Under photolytic conditions, the ethylene ligands are labile and are indeed displaced by the cyclopentadiene. A slow nitrogen purge is used to drive the equilibrium toward the cyclopentadiene complex by removing ethylene from the system. A further photochemical rearrangement occurs: activation of a methylene C-H bond of the coordinated cyclopentadiene. The hydrogen atom is transferred to the $C_5Me_5$ ligand, forming diene complex **297**. A large singlet at δ 4.36 in the $^1$H NMR spectrum of



**79** **296** **297**

(Eq. 103)

the product mixture confirms the presence of an $\eta^5$-cyclopentadienyl ligand. Three methyl signals in the $^1$H NMR spectrum at δ 2.10 (s, 2 Me), δ 1.18 (s, 2 Me) and δ 0.28 (d, $J = 6.1$ Hz, 1 Me) show the disruption of the symmetry of the $\eta^5$-$C_5Me_5$ ligand and formation of the less symmetric $\eta^4$-$C_5Me_5H$ group. The *endo* hydrogen has a characteristic signal at δ 2.48 (quartet, $J = 6.0$ Hz). The infra-red spectrum of the product mixture shows an unusual absorption at 2721 cm$^{-1}$, a frequency normally attributed to the stretching of an *exo* hydrogen atom of a ring complexed to a transition metal.[100] This stretching frequency is therefore attributed to the other isomer: ($\eta^5$-$C_5Me_5$)Co($\eta^4$-$C_5H_6$). The absorption band is quite strong and appears in all IR spectra for complexes of the form ($\eta^5$-$C_5Me_5$)Co($\eta^4$-$C_5H_5R$). This isomer is identified by the large $C_5Me_5$ singlet at δ 1.74 in the $^1$H NMR spectrum. The cyclopentadiene olefin signals are found at 4.75

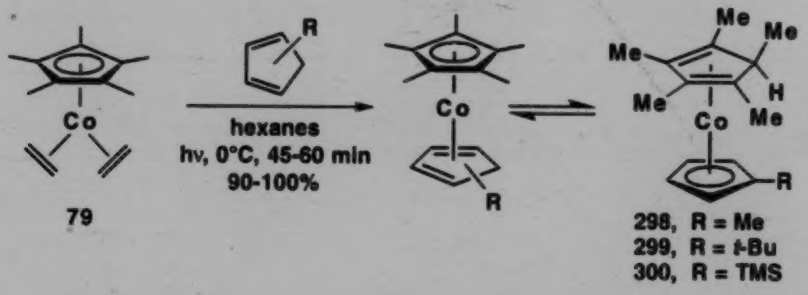
ppm for the internal positions and at 1.76 ppm for the terminal hydrogen atoms of the diene, although this latter signal is partially obscured by the $C_5Me_5$ singlet. The methylene hydrogen atoms resonate at 2.66 and 2.30 ppm and are easily recognizable by integration and their mutual 13.5 Hz coupling constant; however, they show only small (about 1-2 Hz) coupling to the terminal diene protons.

This reaction proved difficult to reproduce exactly; varying mixtures of the two products are obtained, depending on photolysis time and temperature, indicating that a photoequilibium is not necessarily reached under the reaction conditions. Brief optimization attempts show that the hydrogen atom transfer is apparently driven toward the $\eta^4$-pentamethylcyclopentadiene product by photolysis. After prolonged photolysis ($C_6D_6$, 2 h) with a 400 W Hanovia Hg-arc lamp, a 6:1 mixture of the two products is obtained, favoring **297**. By $^1H$ NMR spectroscopy, this ratio does not significantly change after several days at room temperature, suggesting that thermal rearrangement back to the pentamethylcyclopentadienyl complex is either very slow or disallowed. The entire isomerization process thus appears to be photolytic in nature. However, these conclusions are preliminary at best and further study of this isomerization process is warranted.

Molecular orbital calculations have shown that there is a strong antibonding interaction between the metal and the *endo* hydrogen of the methylene in $d^6$-transition metal cyclohexadienyl complexes (Figure **13**, page 138).[175d] The interaction is not as strong in cyclopentadiene complexes, but it is still present. This causes the methylene carbon of the cyclopentadiene ligand to be significantly bent away from the metal and renders the thermal activation of this C-H bond more difficult. However, upon photolysis, this interaction is greatly reduced, and C-H bond activation is more facile. The hydride ligand can then be transferred to the $C_5Me_5$ ring.

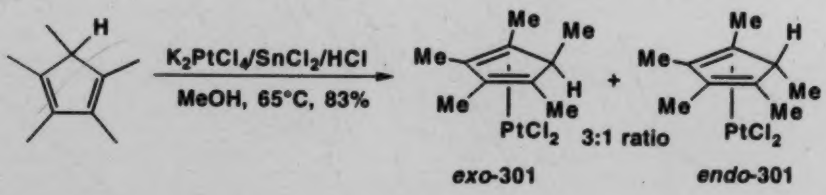
There are several possible reasons why the hydride may transfer to the $C_5Me_5$ ring. Upon transfer, the pentamethylcyclopentadiene structure no longer has five mutually adjacent methyl groups in a planar arrangement; thus, some steric crowding of these buttressed methyl groups is alleviated. Another plausible rationale is that the strongly electron donating $\eta^5$-$C_5Me_5$ ligand places too much electron density onto the already relatively electron rich cobalt(I) center. The stronger interaction with the more weakly electron donating $\eta^5$-$C_5H_5$ ligand is therefore more favorable.

The photochemical reaction of $(\eta^5\text{-}C_5Me_5)Co(C_2H_4)_2$ with substituted cyclopentadienes gives even more complex mixtures (Eq. **104**). Positional isomers of the alkyl-cyclopentadiene ligand are produced, along with the pentamethylcyclopentadiene isomer. Because excess diene is used to trap all of the cobalt starting material, small amounts of cyclopentadiene monomer and dimer may also be present. All products except the unsubstituted complex **297** are obtained as red oils that solidify at -35°C; the parent complex slowly solidifies at room temperature. Due to the high solubility of these complexes in organic solvents, crystallization could not be readily induced, although sublimation is an effective purification for the lower molecular weight complexes **297** and **298**. For simplicity, this mixture of isomers will generally be referred to as the single isomer $(\eta^5\text{-}C_5H_4R)Co(\eta^4\text{-}C_5Me_5H)$, the most prevalent and recognizable isomer, rather than attempting to provide a complete description of each individual mixture.



(Eq. 104)

Other $\eta^4$-pentamethylcyclopentadiene metal complexes are relatively rare, making these complexes highly unusual. A small number of ($\eta^4$-pentamethylcyclopentadiene)iron complexes are known, as well as several other complexes such as $(\eta^5\text{-}C_5Me_5)M(\eta^4\text{-}C_5Me_5H)$ (M = Co, Rh).[224,225] Maitlis and others have reported the preparation of a similar complex, ($\eta^5$-$C_5H_5$)Rh($\eta^4$-$C_5Me_5H$).[226] Most of this chemistry relies upon metal atom vapor synthesis or the reaction of metallicenium cations with hydride sources. Platinum complexes of $\eta^4$-$C_5Me_5H$ (**301**) have been prepared by the direct reaction of metal salts with the free pentamethylcyclopentadiene ligand (Eq. **105**).[227] A similar reactivity pattern has been observed in palladium chemistry.[228] Further reaction of these complexes with TlCp and $TlBF_4$ yields [($\eta^5$-$C_5H_5$)Pt($\eta^4$-$C_5Me_5H$)]$^+$ $BF_4^-$, present as both *endo* and *exo* isomers.[227]

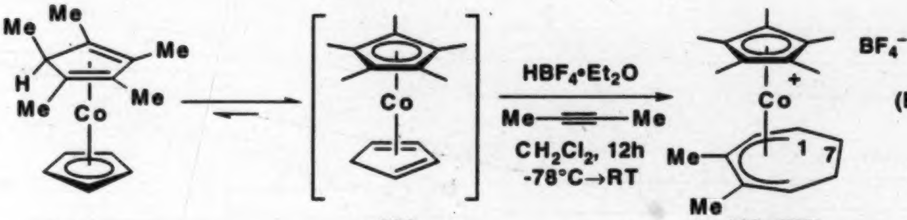


*exo*-**301** *endo*-**301**

(Eq. 105)

### B. *Ring Opening Reactions of Cp*Cobalt Cyclopentadiene Ligands*

To test the proposed mechanism for ring opening, the reaction of the pure pentamethylcyclopentadienyl complex **296** would provide the least complicated results. However, this complex could not be separated from the cyclopentadienyl isomer **297**, so the mixture of isomers was subjected to conditions conducive to ring opening. Protonation with $HBF_4 \cdot Et_2O$ in dichloromethane at -78°C proceeds smoothly in the presence of excess 2-butyne to give dimethylcycloheptadienyl complex **193** in good (70%) yield (Eq. **106**). Pentamethylcobalticenium **302** is obtained as a minor byproduct from dehydrogenation of the cyclopentenyl intermediate. Only the unsubstituted cyclopentadienyl ring appears to undergo cleavage; this indicates that, under these reaction conditions, hydride migrations in the protonated cobalt(III) intermediates are quite facile. Furthermore, it appears that there is an equilibrium that favors formation of the unsubstituted cyclopentenyl intermediate, regardless of the starting isomer, so that only a single insertion product is generated. Thus, the reaction yield is not affected by the use of the isomeric mixture of the starting cyclopentadiene complexes. The cycloheptadienyl complex **193** is identified by several characteristic signals in the $^1H$ NMR spectrum. The pentadienyl fragment is identified by three signals in the $^1H$ NMR spectrum: a doublet at δ 4.67 ($J$ = 9 Hz, $H_2$), a multiplet signal at δ 4.40 ($H_1$), and a doublet of doublets ($J$ = 7.3, 4.0 Hz) at 4.04 ppm ($H_5$). Four signals at 2.45 ($H_{7endo}$), 2.05 ($H_{6endo}$), 1.58 ($H_{7exo}$) and 0.77 ($H_{6exo}$) ppm correspond to the two methylene units. Two quaternary carbon signals are seen in the $^{13}C$ NMR spectrum, at 110.9 ($C_3$) and 107.4 ($C_4$) ppm. Three other carbon signals attributed to $sp^2$-hybridized carbon atoms are present: doublets at δ 97.7 ($C_2$, $^1J_{CH}$ = 165 Hz), 93.5 ($C_1$, $^1J_{CH}$ = 150 Hz) and 87.0 ($C_5$, $^1J_{CH}$ = 156 Hz). In addition, both the HMQC and HMBC spectra strongly support the cycloheptadienyl structure as shown.



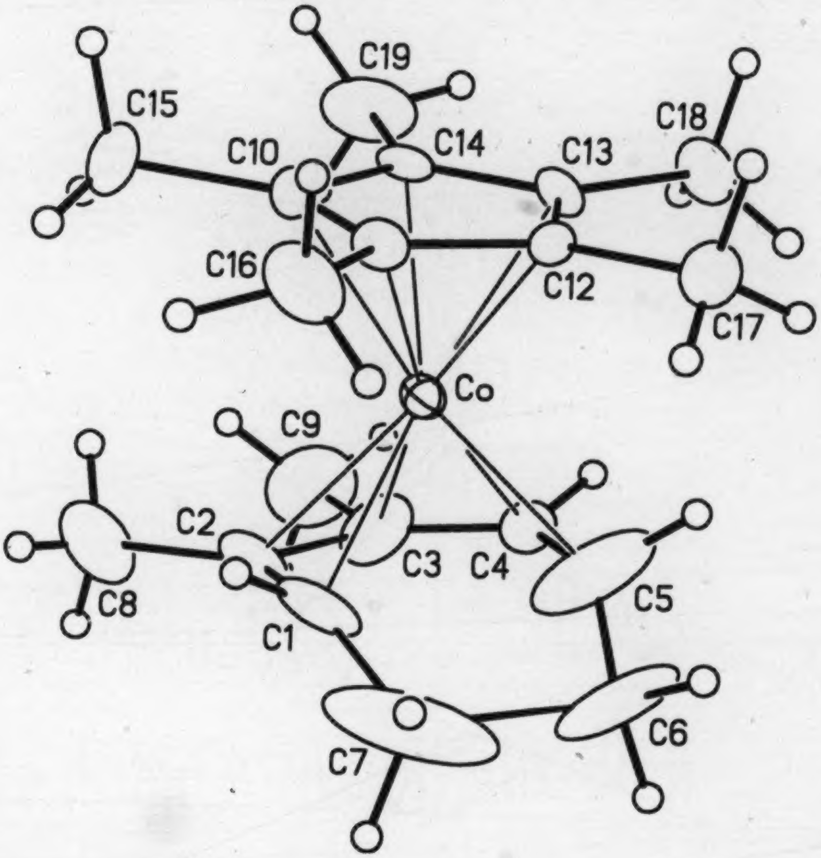
(Eq. 106)

**297** **296** **193**, 70%

+ $[Cp^*CoCp]^+ BF_4^-$
**302**

Although the spectroscopic data unequivocally support the structure of **193**, suitable crystals for X-ray diffraction analysis were grown by layering diethyl ether on top of a solution of **193** in 5% acetonitrile/dichloromethane. The crystals proved to be severely disordered; although the resulting crystal structure can be used to determine atom connectivity, other factors such as bond lengths and angles were not reliably obtained (Figure **14**). Further derivatization of this complex has already been described (Chapter 3, page 110).

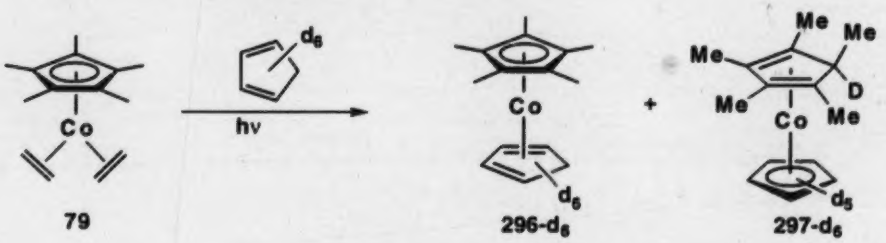
**Figure 14**. ORTEP[115] for Complex **193** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS9605



Final Residuals: $R_1 = 0.0591$; $wR_2 = 0.1371$. Data obtained at -60°C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.
Selected Bond Distances (Å): Co-C1, 2.031(7); ; Co-C2, 2.046(6); Co-C3, 2.060(7); Co-C4, 2.016(6); Co-C5, 2.072(10); C1-C2, 1.335(12); C1-C7, 1.35(2); C2-C3, 1.577(13); C2-C8, 1.419(11); C3-C4, 1.352(14); C3-C9, 1.451(12); C4-C5, 1.341(12); C5-C6, 1.356(15); C6-C7, 1.80(3).

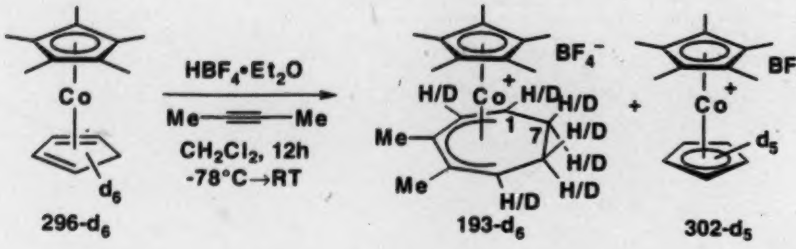
Selected Bond Angles (deg.): C2-C1-C7, 146.4(16); C1-C2-C3, 112.9(7); C1-C2-C8, 133.7(11); C3-C2-C8, 113.2(9); C2-C3-C4, 119.7(7); C2-C3-C9, 114.1(10); C4-C3-C9, 125.5(11); C3-C4-C5, 123.0(11); C4-C5-C6, 144.1(13); C5-C6-C7, 100.3(10); C1-C7-C6, 107.4(13)

To provide more information on the reactivity of the proposed cyclopentenyl intermediate, the reaction of ($\eta^5$-$C_5Me_5$)Co($\eta^4$-$C_5H_6$) (**296**) with DOTf in the presence of 2-butyne was investigated, with the expectation that some deuterium scrambling would be observed. The triflate counterion strongly affects this reactivity pattern, as pentamethylcobalticenium complex **302** is obtained as the major product; no seven-membered ring is observed by TLC analysis or by $^1$H NMR spectroscopy. Since deuterated $HBF_4$ is not readily available, the opposite labeling study was undertaken; the reaction of the perdeuterated cyclopentadiene ligand with $HBF_4$•$Et_2O$. Hexadeuterated cyclopentadiene was prepared according to the literature procedure[229] and reacts with ($\eta^5$-$C_5Me_5$)Co($C_2H_4$)$_2$ to yield the deuterated complexes **296**-$d_6$ and **297**-$d_6$ (Eq. **107**), as deduced from $^1$H and $^2$H NMR spectroscopy.



(Eq. 107)

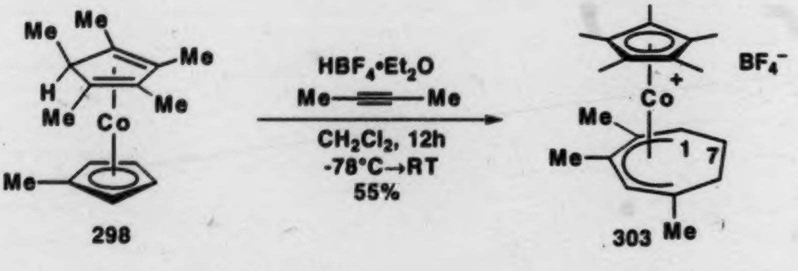
The reaction of **296**-$d_6$ with $HBF_4$•$Et_2O$ and 2-butyne in dichloromethane gives both alkyne insertion and dehydrogenation products (Eq. **108**). Spencer reports that the protonation of CpCo(norbornadiene) occurs initially at the cobalt center.[128a] Based on this result, it was expected that the hydrogen atom would be observed only at the 6-*endo* and 7-*endo* positions. However, the $^1$H NMR spectrum of complex **193-d$_6$** shows significant amount of protium content in all positions except the two *exo* positions, although the resolution at these latter signals is poor. These signals are normally quite broad and in the hydrogen-depleted complex, may be lost in the baseline noise. Although we anticipated that $^2$H NMR spectroscopy would show no signals for the 6-*endo* and 7-*endo* positions, the data show that each position is partially and equivalently deuterated.


HBF$_4$•Et$_2$O
Me—≡—Me
CH$_2$Cl$_2$, 12h
-78°C→RT
Co
d$_6$
296-d$_6$
BF$_4^-$
H/D
H/D
H/D
H/D
H/D
H/D
H/D
Me
Me
1
7
193-d$_6$
+
d$_5$
302-d$_5$

(Eq. 108)

These results are not readily rationalized. Protonation exclusively at the metal center cannot explain the extensive scrambling of the proton "label". In contrast, protonation on the *exo* face of the cyclopentadiene ligand would result in scrambling everywhere except the 6-*endo* and 7-*endo* positions. However, since the 7-*endo* position is clearly visible in the $^1$H NMR spectrum, some of the hydrogen "label" must be placed there. Consequently, there must be some mechanism for exchanging the *endo* and *exo* hydrogen atoms other than β-hydrogen elimination reaction at the metal center. Rational possibilities include a [1,5]-hydride shift or deprotonation by an external base (presumably diethyl ether), followed by reprotonation at the metal. These phenomena have not been conclusively demonstrated and further study of this reaction is warranted.

Substituted cyclopentadiene complexes also undergo similar ring expansion reactions (Table 8). Methylcyclopentadiene complex **298** (along with its isomer), upon reaction with HBF$_4$•Et$_2$O and 2-butyne in CH$_2$Cl$_2$, generates the 2,3,5-trimethylcycloheptadienyl complex **303** in 55% isolated yield (Eq. **109**) after purification by flash chromatography. The trimethylcycloheptadienyl pattern is established by the observation of only two downfield signals in the $^1$H NMR spectrum at δ 4.80 (s, H$_4$) and


Me
Me
Me
H
Me
Me
Co
Me
298
HBF$_4$•Et$_2$O
Me—≡—Me
CH$_2$Cl$_2$, 12h
-78°C→RT
55%
BF$_4^-$
+
Co
Me
Me
1
7
Me
303

(Eq. 109)

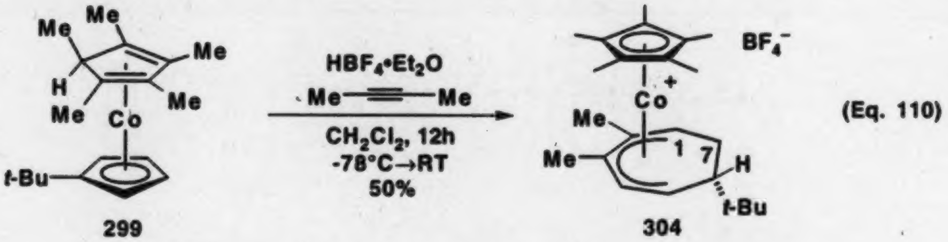
**Table 8**. Comparative $^1$H NMR Spectroscopic Data For Cp* $\eta^5$-Cycloheptadienyl Complexes Derived from Ring Opening Reactions of Cp*Co(1-R-Cyclopentadiene)

| | 193 | 303 | 304 | 309 | 310 |
|---|---|---|---|---|---|
| **$H_1$**<br>$J_{1\text{-}2}$ | 4.40 (ddd)<br>9.0 Hz | 3.91 (dd)<br>b | 4.05 (dd)<br>b | 3.98 (d)<br>b | 4.29 (ddd)<br>10 Hz |
| **$H_2$**<br>$J_{2\text{-}3}$ | 4.67 (br.d)<br>NA | b | b | b | 4.59 (d)<br>b |
| **$H_3$**<br>$J_{3\text{-}4}$ | b | b | b | b | b |
| **$H_4$**<br>$J_{4\text{-}5}$ | b | 4.80 (br s)<br>b | 5.00 (d)<br>8.3 Hz | 5.08 (d)<br>8.2 Hz | b |
| **$H_5$**<br>$J_{5\text{-}6endo}$<br>$J_{5\text{-}6exo}$ | 4.04 (dd)<br>4.0 Hz<br>7.3 Hz | b | 4.15 (dd)<br>5.0 Hz | 4.26 (ddd)<br>8.0 Hz<br>4.4 Hz | 3.82 (dd)<br>8.4 Hz<br>4.5 Hz |
| **$H_{6endo}$**<br>$J_{6endo\text{-}6exo}$<br>$J_{6endo\text{-}7endo}$<br>$J_{6endo\text{-}7exo}$ | 2.00 (m)<br>16.5 Hz<br>9 Hz<br>a | 1.67$^b$ (m)<br>14.5 Hz<br>7.9 Hz<br>a | 0.21 (ddd)<br>b<br>11.8 Hz<br>5.3 Hz | 2.0 (m)<br>13.8 Hz<br>b<br>a | 1.8 (m)<br>12.6 Hz<br>b<br>a |
| **$H_{6exo}$**<br>$J_{6exo\text{-}7endo}$<br>$J_{6exo\text{-}7exo}$ | 0.77 (dddd)<br>8 Hz<br>5.9 Hz | 0.70 (ddd)<br>8.1 Hz<br>5.5 Hz | b | 0.19 (dddd)<br>b<br>9.6 Hz | -0.14 (ddd)<br>b<br>10.5 Hz |
| **$H_{7endo}$**<br>$J_{7endo\text{-}7exo}$<br>$J_{7endo\text{-}1}$ | 2.45 (dddd)<br>15.9 Hz<br>4.5 Hz | 2.50 (dddd)<br>16.7 Hz<br>4.6 Hz | 2.64 (ddd)<br>16.0 Hz<br>3.5 Hz | b | b |
| **$H_{7exo}$**<br>$J_{7exo\text{-}1}$ | 1.58 (dddd)<br>3.3 Hz | 1.67$^b$ (m)<br>a | 2.15 (ddd)<br>3.5 Hz | 2.8 (m)<br>3.6 Hz | 2.8 (m)<br>3.6 Hz |

[a] Numerical value for the coupling constant was not obtained due to second order character or complexity of the signal. [b] Not applicable due to a non-hydrogen substituent.

3.91 (dd, $J = 7.3, 4.0$ Hz, $H_1$). Other signals pertaining to the methylene units of the seven-membered ring are also present, fitting the general pattern observed for the spectra of cycloheptadienyl products (Table **8**).

The reaction of *t*-butylcyclopentadienyl complex **299** with $HBF_4 \cdot Et_2O$ and 2-butyne in $CH_2Cl_2$ forms the cycloheptadienyl complex **304** in 50% yield (Eq. **110**). As previously observed in the product obtained from the reaction of crotyl triflate complex **85** with *t*-butylacetylene (Chapter **4**, Eq. **96**, page 155), the *t*-butyl group in complex **304** is found on an $sp^3$-hybridized carbon of the cycloheptadienyl ring. This presumably reflects a preference to place the large *t*-butyl group away from the metal center. The substitution pattern of this seven-membered ring product is revealed by the three typical signals in the $^1H$ NMR spectrum at 5.00 ($H_4$), 4.15 ($H_5$), and 4.05 ($H_1$) ppm, characterizing the pentadienyl framework. In addition, only three upfield signals are observed resonating at 2.64 ($H_{7endo}$), 2.15 ($H_{7exo}$), and 0.21 ($H_6$) ppm. Since both methyl groups are singlets at $\delta$ 2.24 and $\delta$ 1.88, they must be on the pentadienyl fragment; thus, it is the *t*-butyl group that is attached to $C_6$.

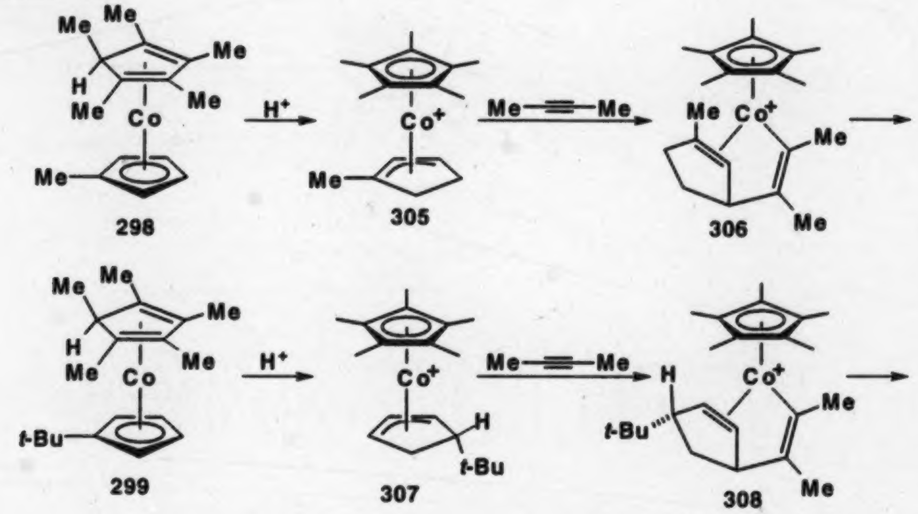


(Eq. 110)

Since only a single product is obtained in both of these reactions, only one substituted cyclopentenyl isomer is formed or is kinetically trapped by the alkyne. With methylcyclopentadiene, the product substitution pattern reveals that the 1-methylcyclopentenyl intermediate **305** is formed, consistent with inductive stabilization of the allyl ligand by the methyl group (Scheme **58**). However, the reaction of *t*-butylcyclopentadiene apparently leads to a different cyclopentenyl isomer, **307**, with the *t*-butyl group located off the allylic framework. It is likely that the steric profile of a 1-*t*-

butyl group destabilizes coordination of the cyclopentenyl through interaction with the large Cp* ligand. This steric strain is alleviated by placing the *t*-butyl group *exo* to the metal center. Both cyclopentenyl intermediates **305** and **307** insert the alkyne in the less substituted side of the allyl framework, generating vinyl alkene intermediates **306** and **308**, respectively. The conversion of the vinyl alkene complexes to cycloheptadienyl products has been previously discussed (see Chapter 4, Section 2, page 165).

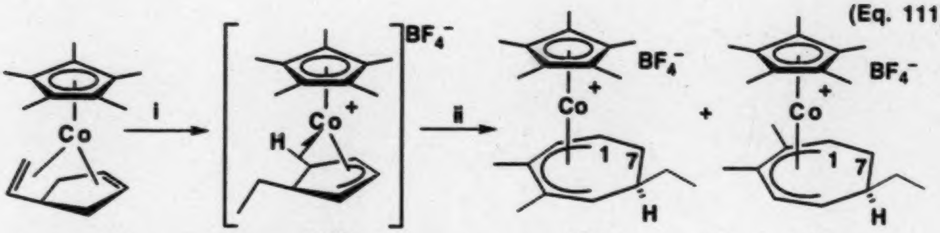
**Scheme 58**



As also previously discussed, Spencer reports ring opening upon protonation of a cyclopentadiene complex.[128] In his system, an agostic ethylcyclopentenyl intermediate is formed at temperatures slightly above 0°C, although ring opening is not observed until much higher temperatures. We were interested to determine the competency of this agostic complex in our ring opening reaction.

Following Spencer's procedure, $(\eta^5\text{-}C_5Me_5)Co(\eta^4\text{-4-vinylcyclopentene})$ was synthesized starting from norbornadiene.[128] Protonation of this complex using $HBF_4{\bullet}Et_2O$ at -78°C in $CH_2Cl_2$ was carried out and the solution allowed to warm to room temperature for 2 h, after which it was re-cooled to -78°C. This procedure was intended to allow the protonated complex to rearrange to agostic intermediate **173**, as shown in Eq. **111**. Addition of excess 2-butyne at -78°C did not induce a noticeable color change. However, after slow warming to room temperature and chromatographic work-up, a 1:1 ratio of regioisomeric cycloheptadienyl complexes **309** and **310** was isolated in low yield (Eq. **111**).

(Eq. 111)

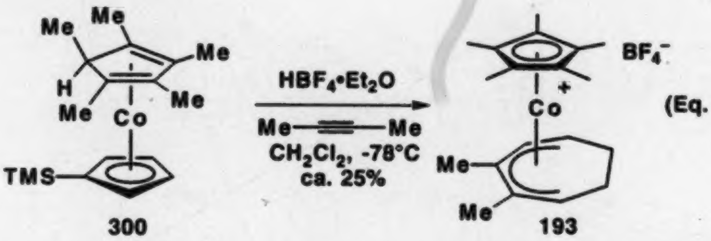


**173** **309** 1:1 **310**

**Conditions: (i) $HBF_4{\cdot}Et_2O$, $CH_2Cl_2$, -78°C→RT. (ii) 2-butyne, $CH_2Cl_2$, -78°C→RT, 12h, 36%**

Because this reaction could not be followed by $^1H$ NMR spectroscopy, due to the formation of paramagnetic material, it is difficult to draw any definite conclusions. However, the agostic interaction does not prevent this reaction and the 2-butyne apparently inserts equally into either terminus of the cyclopentenyl ligand in **173**, generating the isomeric cycloheptadienyl complexes. Note that this result differs slightly from the reaction of the methylcyclopentadiene complex **298**; the ethyl group is positioned on the *endo* face, preventing positional isomerization by β-hydride elimination/re-insertion reactions. The methyl group in **298**, in contrast, does not hinder β-hydride elimination induced rearrangements and the cyclopentenyl ligand is fully fluxional. The presence of the methyl group on the cyclopentenyl intermediate also inhibits the alkyne from inserting into that position; this results in the formation of only one isomer. The *endo* ethyl group apparently has little effect on the alkyne insertion regioselectivity and, as a result, the alkyne inserts into either end of the cyclopentenyl intermediate. It is also interesting that the ring-opening reaction that yields cycloheptadienyl complexes **309** and **310** proceeds at ambient temperatures or lower, but the direct C-C activation of **173** occurs only at elevated (60°C) temperature.

Other substituents on the cyclopentadiene ligand, such as the trimethylsilyl group, are less successful in the production of seven-membered ring products. Trimethylsilylcyclopentadiene complex **300** does react with $HBF_4 \cdot Et_2O$ and 2-butyne, but the reaction is not clean. The only product isolated after chromatography is the desilylated dimethylcycloheptadienyl complex **193** (Eq. **112**) in about 25% yield. It is not clear if the desilylation occurs during the reaction or during the chromatography. However, other cycloheptadienyl complexes containing trimethylsilyl groups on the pentadienyl portion of the cycloheptadienyl ring are stable to both the acidic reaction conditions and silica gel chromatography (*vide infra*). This suggests that the (trimethylsilyl)cyclopentenyl intermediate formed in the reaction may have the $SiMe_3$ group attached to a $sp^3$ carbon center, similar to the *t*-butyl substituted case (**304**). The $Csp_3$-Si bond must more readily protodesilylate than the $Csp_2$ -Si bond in order to observe only desilylated product.

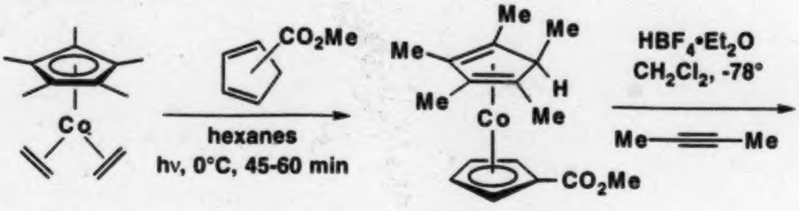


**300**

**193**

(Eq. 112)

Only electron donating substituents on the cyclopentadiene ligand have been evaluated thus far. To test for electronic effects and to introduce greater functionality, carbomethoxycyclopentadiene complex **311** was synthesized (Eq. **113**). This complex, upon reaction with $HBF_4 \cdot Et_2O$ and 2-butyne, forms a mixture of unidentified products. The only isolable compound, produced in low yield, appears to be the cobalticenium complex, identified by TLC analysis. Carbomethoxycyclopentadiene reacts with $(C_5Me_5)Co(C_2H_4)_2$ under photolytic conditions to give a mixture of isomers, which was characterized by mass spectrometry and used directly in the next step.

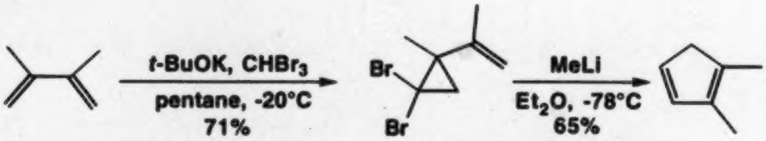


(Eq. 113)

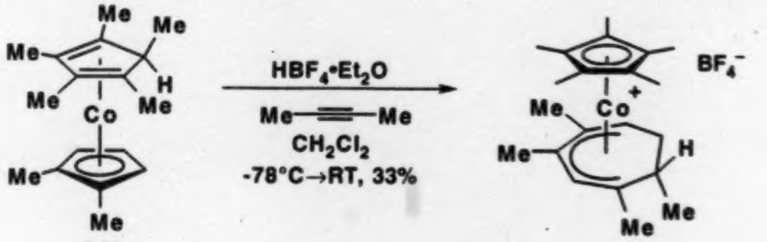
79 311

Another test for the proposed abnormal [3 + 2 + 2] reaction pathway is the reaction of the dimethylcyclopentadiene derivative ($\eta^5$-$C_5H_3Me_2$)Co($\eta^4$-$C_5Me_5H$) **312** with $HBF_4$•$Et_2O$ in the presence of 2-butyne, intercepting the putative intermediate formed in the reaction of allyl complex **80** with 2-butyne. 1,2-Dimethylcyclopentadiene was prepared using the procedure of Boag, in which 2,3-dimethylbutadiene is cyclopropanated using *t*-BuOK and bromoform (Scheme **59**).[230] The resulting 1,1-dibromo-2-methyl-2-isopropenylcyclopropane reacts with MeLi to provide 1,2-dimethylcyclopentadiene after aqueous workup.

**Scheme 59**



1,2-Dimethylcyclopentadiene reacts with ($\eta^5$-$C_5Me_5$)Co($C_2H_4$)$_2$ (**79**) under photolytic conditions to produce the red, oily, air sensitive product dimethylcyclopentadienyl complex **312**, which was used without characterization. Protonation of this complex with $HBF_4$•$Et_2O$ in the presence of 2-butyne gives the red tetramethylcycloheptadienyl complex **87** (Eq. **114**) in modest yield, identical by $^1$H NMR spectroscopy to the tetramethylcycloheptadienyl complex prepared from ($\eta^5$-$C_5Me_5$)Co($\eta^3$-$C_3H_5$)(OTf) (**80**) and 2-butyne. Thus the five-membered ring cyclopentenyl complex is a competent intermediate in the formation of **87** from allyl triflate **80** and 2-butyne. The large discrepancy in the yield of this process relative to the [3 + 2 + 2] allyl/2-butyne cycloaddition reaction presumably is due to the greater number of hydrogen transfer processes required to form the final cycloheptadienyl product and to the use of crude uncharacterized **312** in this reaction. Both the hydride from the $C_5Me_5H$ ligand and the $HBF_4$ must eventually migrate to the dimethylcyclopentadienyl ring.



312

87

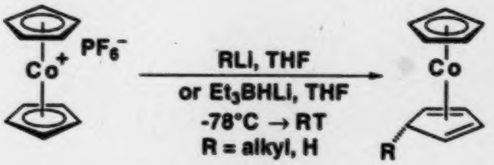
(Eq. 114)

Incorporation of other alkynes into this reaction process was attempted without notable success. It is possible that larger disubstituted alkynes have a more difficult steric barrier to overcome, hindering coordination. This favors the dehydrogenation pathway, giving the cobalticenium product. The sole exception to this trend is the reaction of ($t$-Bu-$C_5H_4$)Co($\eta^4$-$C_5Me_5H$) (**299**) with $HBF_4$•$Et_2O$ in $CH_2Cl_2$ in the presence of *t*-butylacetylene. This reaction has a two-fold significance. This is the only example in which the ($C_5Me_5$)Co template reacts resonably cleanly with an alkyne other than 2-butyne. In addition, greater insight into the partitioning between the "normal" [3 + 2 + 2] cycloaddition and this new [5 + 2] reaction can be obtained from this reaction as well.

The reaction of Cp*allyl triflate complex **80** with *t*-butylacetylene can be readily rationalized by the previously proposed [3 + 2 + 2] cycloaddition mechanism, although the substitution pattern is somewhat unusual (*cf.*, Chapter 2, page 45). In order to evaluate the possibility that this reaction proceeds via a [5 + 2] mechanism, the reaction of *t*-butylcyclopentadienyl complex **299** with $HBF_4$•$Et_2O$ and *t*-butylacetylene was conducted. In this reaction a red product is obtained in low yield, tentatively identified as a different cycloheptadienyl complex than that obtained previously, but the reaction does not proceed cleanly enough to conclusively identify the product. This result nonetheless suggests that the reaction of the Cp*Co allyl triflate complex **80** with *t*-butylacetylene does in fact proceed via a "normal" [3 + 2 +2] allyl/alkyne cycloaddition process.

### *C. Ring Opening Reactions of Methylcyclopentadienyl Cobalt Cyclopentadiene Ligands*

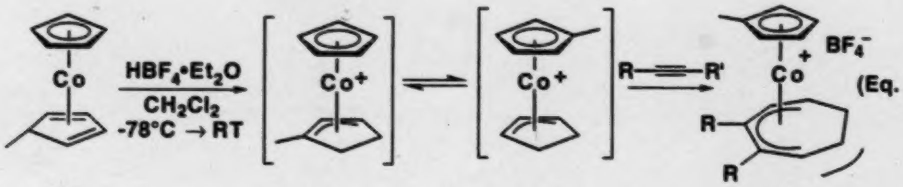
Due to the apparent steric limitations of the Cp* template, other, less sterically hindered systems were evaluated for mediating this unprecedented [5 + 2] cycloaddition . Various methods have been used for the synthesis of cyclopentadienyl cobalt cyclopentadiene systems. The parent system, $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_5H_6)$ **313**, was synthesized as early as 1959 by sodium borohydride reduction of the cobalticenium cation.[231] Methodology used to synthesize alkylcyclopentadiene complexes includes the reaction of the neutral cobaltocene with halocarbons or $R_2Cd$ and the reaction of cobalticenium salts with $R_3Al$ or RM (M = Li, Na, K, MgX).[93g,232-235] The latter method is perhaps the most widely used, due to the ready availability of commercial alkyllithium and alkylmagnesium halide compounds, as well as various cobalticenium complexes. Using a range of alkyllithium and Grignard reagents, alkylcyclopentadiene complexes $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_5H_5R)$ (R = H, Me, *i*-Pr, *t*-Bu), were prepared in high yield from cobalticenium hexafluorophosphate (Eq. **115**). All these known compounds are obtained as red, air sensitive solids (R = H, *t*-Bu) or oils (R = Me, *i*-Pr).[93g]



**313**, R = H
**314**, R = Me
**315**, R = *i*-Pr
**316**, R = *t*-Bu

(Eq. 115)

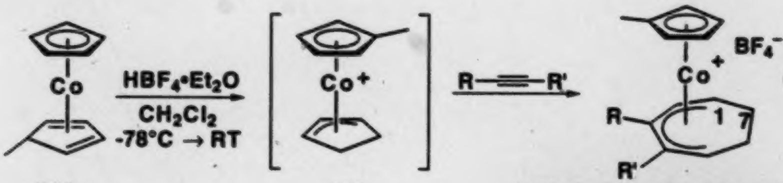
Initial studies using the unsubstituted complex **313** showed no tendency for the cyclopentenyl intermediate to incorporate alkyne: protonation of $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_5H_6)$ in the presence of alkyne returns only cobalticenium tetrafluoroborate. However, the methyl substituted complex, ($\eta^5$-$C_5H_5$)Co($\eta^4$-1-Me-$C_5H_5$) (**314**), reacts with $HBF_4$•$Et_2O$ in the presence of alkynes to form seven-membered ring complexes in high yields (Eq. **116**). There is a considerable preference for the formation of a single cycloheptadienyl complex; that is, only the less substituted cyclopentenyl ring reacts. Although protonation of the diene complex **314** might be expected to form intermediate **317**, it apparently isomerizes to the unsubstituted $\eta^3$-cyclopentenyl **318**, which then coordinates and inserts alkyne to give the final ($\eta^5$-methylcyclopentadienyl)cobalt($\eta^5$-cycloheptadienyl) cations **319** (*vide infra*).



(Eq. 116)

**314** **317** **318** **319**

The reactions of other alkynes with this intermediate produce only ring-expanded methylcyclopentadienyl complexes, as only the smaller ring reacts. The reaction of *t*-butylpropyne, trimethylsilylpropyne, or bis(trimethylsilyl)acetylene with *in situ* protonated ($C_5H_5$)Co($\eta^4$-$C_5H_5$Me) produces cycloheptadienyl complexes **320-322**, respectively, in high yield (Eq. **117**). All of these compounds are fully characterized orange or red solids.



(Eq. 117)

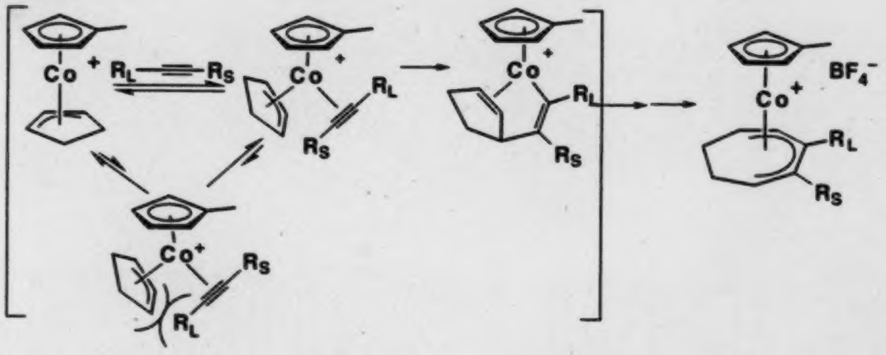
**314** **318**

**320, R, R' = *t*-Bu, Me: 85%**
**321, R, R' = TMS, Me: 85%**
**322, R, R' = TMS: 94%**

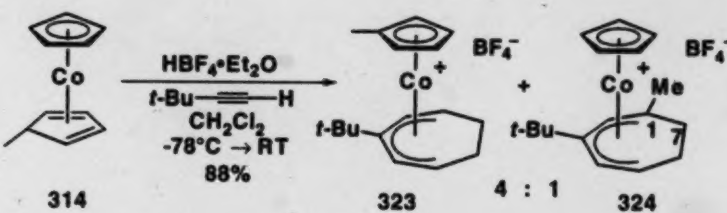
The $^1$H NMR spectra for these methylcyclopentadienyl complexes are remarkably similar and conform to the general patterns established for $\eta^5$-cycloheptadienyl complexes (Table **9**). In particular, the observed values of the coupling constants are very similar in these complexes.

A common characteristic of the 3,4-disubstituted cycloheptadienyl complexes is the strong preference to place the largest substituent on the central position of the ring. This, we believe, arises in the transition state for insertion, from the preferred orientation of the alkyne in the coupling to the cyclopentenyl ligand (Scheme **60**). This presumably reflects a kinetic preference of the cyclopentenyl to migrate to the least hindered side of the alkyne, resulting in placement of the larger group next to the metal.

**Scheme 60**



There is, however, some evidence that this is a delicately balanced system. Protonation of methylcyclopentadiene complex **314** in the presence of *t*-butylacetylene yields two cycloheptadienyl products in a 4:1 ratio (Eq. **118**). The minor product **324**



**314** **323** **324**

(Eq. 118)

arises from ring opening of the methylcyclopentenyl ligand, whereas the major cycloheptadienyl complex **323** results from the cleavage of the unsubstituted cyclopentadienyl ligand. Since the reactions of cyclopentadiene complex **314** with

**Table 9**. Comparative $^{1}H$ NMR Spectroscopic Data for Methylcyclopentadienyl Derived Cycloheptadienyl Complexes

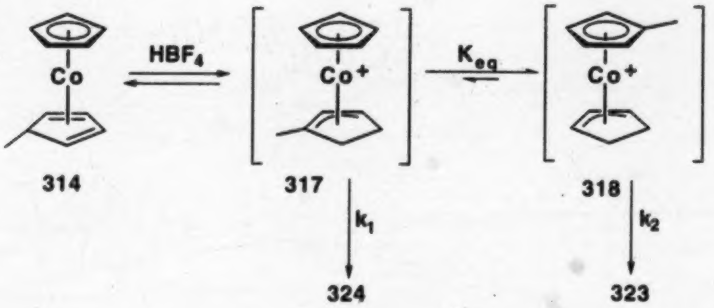
| | **320** | **321** | **322** | **323** | **325** |
|---|---|---|---|---|---|
| $\mathbf{H_1}$ | 5.27 (m) | 5.35 (m) | 5.70 (m) | 5.15 (m) | 5.35 (m) |
| $J_{1\text{-}2}$ | 9.6 Hz | 9.6 | 10.2 | 9.0 Hz | a |
| $\mathbf{H_2}$ | 5.17 (m) | 5.09 (d) | 5.08 (d) | 5.46 (d) | 5.35 (m) |
| $J_{2\text{-}3}$ | b | b | b | b | b |
| $\mathbf{H_3}$ | b | b | b | b | b |
| $J_{3\text{-}4}$ | | | | | |
| $\mathbf{H_4}$ | b | b | b | 5.46 (d) | b |
| $J_{4\text{-}5}$ | | | | 9.0 Hz | |
| $\mathbf{H_5}$ | 4.96 (dd) | 5.01 (dd) | 5.23 (dd) | 5.15 (m) | 5.63 (dd) |
| $J_{5\text{-}6endo}$ | 8.4 | 8.1 | 8.1 | a | 8.1 |
| $J_{5\text{-}6exo}$ | 5.4 | 5.1 | 5.6 | a | 4.8 |
| $\mathbf{H_{6endo}}$ | 1.70 (m) | 1.85 (m) | 1.65 (m) | 2.45 (m) | 2.29 (m) |
| $J_{6endo\text{-}6exo}$ | 12.5 | 12.2 | 12.6 | a | 13.6 |
| $J_{6endo\text{-}7endo}$ | 8.3 | 8.3 | 8.3 | a | 9.0 |
| $J_{6endo\text{-}7exo}$ | 0.8 | 0.8 | 2.1 | a | 2.5 |
| $\mathbf{H_{6exo}}$ | 0.057 | 0.15 (m) | 0.04(dddd) | 1.20 (m) | 0.79 (m) |
| $J_{6exo\text{-}7endo}$ | 11.6 | 12.0 | 12.6 | a | 10.0 |
| $J_{6exo\text{-}7exo}$ | 5.7 | 5.9 | 5.9 | a | 5.1 |
| $\mathbf{H_{7endo}}$ | 2.87 (dddd) | 2.94 (m) | 3.09 (m) | 2.45 (m) | 3.08 (dddd) |
| $J_{7endo\text{-}7exo}$ | 17.4 | 17.5 | 18.0 | a | 17.5 |
| $J_{7endo\text{-}1}$ | 3.6 | 3.9 | 3.6 | a | 0.8 |
| $\mathbf{H_{7exo}}$ | 1.98 (m) | 2.00 (m) | 2.20 (m) | 1.20 (m) | 2.02 (dd) |
| $J_{7exo\text{-}1}$ | 2.0 | small | 3.2 | a | <2 Hz |

[a] Numerical value for the coupling constant was not obtained due to second order character or complexity of the signal. [b] Not applicable due to a non-hydrogen substituent.

$HBF_4{\bullet}Et_2O$ and other alkynes yield only single products, this particular example is unique: an informative, but unusual process.

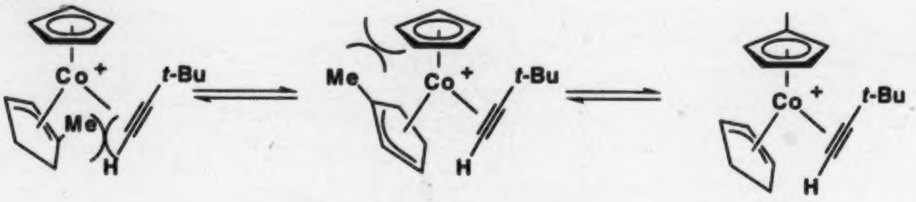
There are two factors to consider in the formation of cycloheptadienyl complexes **323** and **324**, depending on the thermodynamic and kinetic parameters for the interconversion of the cyclopentenyl intermediates. Although there must be a series of β-H elimination/ reinsertion equilibria to convert intermediate **317** to **318**, the thermodynamic preference is unknown. Given the product distribution, either the equilibrium favors intermediate **318** (*i.e.*, $K_{eq} > 1$), or the rate of reaction of **318** with alkyne is faster than the reaction of **317** with alkyne (*i.e.*, $k_2 > k_1$) (Scheme **61**).

**Scheme 61**

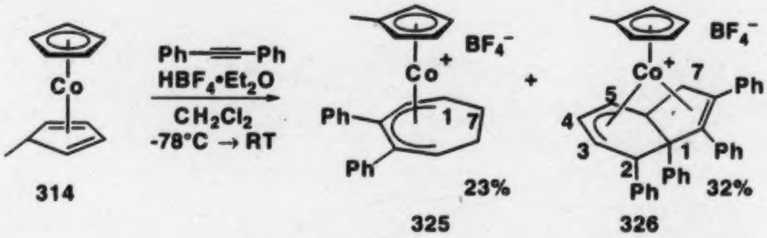


It seems unlikely that the equilibrium would be shifted dramatically to one side, as the thermodynamic stability of **317** and **318** appear to be comparable. However, a preferential reaction with the less sterically encumbered cyclopentenyl intermediate **318** seems to be a reasonable proposal. As depicted in Scheme **62**, the steric interaction between the alkyne and a terminal R group on the cyclopentenyl ligand may be significant, inhibiting insertion reactions while in this geometry. A slightly less severe steric interaction is noted between the alkyl group on the cyclopentenyl ligand and the cyclopentadienyl ligand, whereas the least hindered scenario occurs with the alkyl group on the cyclopentadienyl ligand, where the cyclopentadienyl ring is free to rotate. The other alkynes evaluated are all disubstituted and would be expected to coordinate less well to the methylcyclopentenyl intermediate **317**; instead they may coordinate preferentially to the unsubstituted cyclopentenyl **318**. Thus, *t*-butylacetylene alone is reactive enough to trap some of the methylcyclopentenyl intermediate **317** present in the equilibrium mixture. Other alkynes, in contrast, react exclusively with the smaller cyclopentenyl intermediate.

**Scheme 62**



The reaction with diphenylacetylene gives a low yield of an orange solid tentatively characterized as the diphenylcycloheptadienyl complex **325** (Eq. **119**). The major product obtained from this reaction arises from a unique pathway. A light brown solid, tentatively assigned as bicyclic double insertion product **326** (Eq. **119**) is isolated in 32% yield after chromatographic separation. Due to the complexity of the spectral data,



(Eq. 119)

the structural assignment is quite tentative and the mechanistic proposal is entirely speculative. However, it is quite clear that two equivalents of the alkyne are incorporated, based on integration of the phenyl region in the $^1$H NMR spectrum and number of signals in the $^{13}$C spectrum. In addition, the electrospray mass spectrum of the product shows the parent ion (m/z = 561.198751) corresponds to a formula of $C_{39}H_{34}Co^+$, consistent only with a double alkyne adduct.

The $^1H$ NMR spectrum for complex **326** contains the expected broad singlets for the methylcyclopentadienyl ligand that resonate at 5.24 (1H), 4.91 (2H), 4.50 (1H) and 1.64 (3H) ppm. In the HMQC spectrum, these signals correlate to carbon signals at 88.5, 94.2, 93.2, 95.6 and 12.6 ppm, respectively. Furthermore, the downfield carbon resonances show $^1J_{CH}$ values of 186, 177, 186, and 183 Hz, respectively, while the methyl signal has a $^1J_{CH}$ value of 128 Hz. The remaining quaternary carbon is found at 104.2 ppm.

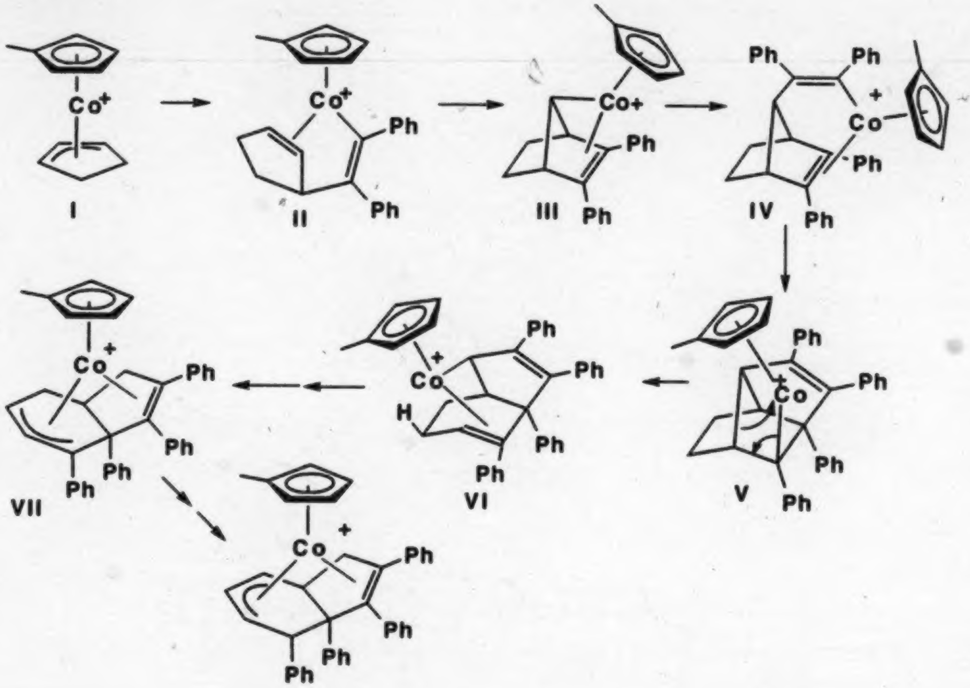
The structure for the other ligand is more difficult to determine. Only one signal with a large geminal coupling constant of 15 Hz is observed in the $^1H$ NMR spectrum, connecting two signals that resonate at $\delta$ 3.31($H_{7b}$) and $\delta$ 4.19 ($H_{7a}$). These are relatively far downfield for protons on an $sp^3$-hybridized carbon, but the HMQC spectrum proves that $C_7$ is $sp^3$ hydridized and that it is attached to both $H_7$ protons. Although $H_{7a}$ appears to be a simple broad doublet, $H_{7b}$ has a further small coupling constant of 3.0 Hz, connecting it to $\delta$ 2.77 ($H_6$). The COSY spectrum shows correlations from both $H_7$ signals to $H_6$ only, suggesting the presence of a tetrasubstituted carbon adjacent to $C_7$. The $H_6$ signal, in contrast, correlates to a signal at $\delta$ 6.35 ($H_5$) in the COSY spectrum, but again, does not have an appreciable coupling constant value. The $H_5$ proton is a broad doublet ($J$ = 6 Hz), which is suggestive of the small couplings to $H_6$ and $H_3$ observed in the COSY spectrum and a larger coupling to $\delta$ 5.11 ($H_4$). The $H_4$ signal is in turn correlated to a signal shifted strongly downfield to about 6.89 ppm and obscured by the phenyl protons. However, this obscured signal is coupled to the last ring proton, a doublet ($J$ = 5 Hz), which resonates at $\delta$ 4.35 ($H_2$). The HMQC spectrum correlates these six mutually coupled protons to the following carbon signals: 91.7 (d, $^1J_{CH}$ = 171.1 Hz, $C_4$), 91.5 (d, $^1J_{CH}$ = 169.7 Hz, $C_5$), 81.8 (d, $^1J_{CH}$ = 168.2 Hz, $C_3$), 52.4 (d, $^1J_{CH}$ = 131.1 Hz, $C_2$), 48.0 (t, $^1J_{CH}$ = 126.6 Hz, $C_7$), and 38.6 (d, $^1J_{CH}$ = 138.8 Hz, $C_6$).

The value of the $^1J_{CH}$ coupling constant further demands that $C_3$, $C_4$ and $C_5$ are $sp^2$-hybridized and the chemical shift data suggest that these three carbon atoms are coordinated to cobalt to form a π-allyl fragment. The downfield shift of $H_2$ relative to $H_6$ suggests a phenyl substituent. A key piece of data is the carbon signal that resonates at δ 64.0, shown to be quaternary by both the HMQC spectrum and the gated decoupled $^{13}C$ NMR spectrum. The HMBC spectrum shows this carbon is correlated to both the $H_3$ and $H_5$ protons. This can only arise if $C_1$ is attached to $C_6$ and $C_2$ to form a six-membered ring, as the HMBC spectrum shows only $^3J_{CH}$ and $^2J_{CH}$ relations. The $C_1$-$H_5$ correlation thus cannot be through the $C_1$-$C_2$-$C_3$-$C_4$-$C_5$-$H_5$ linkage, a five-bond correlation, but must be through the $C_1$-$C_6$-$C_5$-$H_5$ link, a three-bond correlation.

A quick count of the remaining atoms reveals only a diphenylacetylene unit remains to be placed into the structure. Since there are still unfilled "coordination" sites on $C_1$ and $C_7$, the diphenylacetylene unit must join these two positions, completing the five-membered ring fragment. Although only a single carbon signal ($C_9$) in this last piece is located and assigned, it supports the proposed structure. In the HMBC spectrum, the $C_9$ carbon is correlated to $H_2$ and $H_{7a}$, both three-bond relations.

The mechanism for this transformation is obviously of some concern, although there is only this one example. All other ring-opening reactions (with the exception of reactions with acetylene, to be discussed shortly) proceed in good to excellent yield to the 3,4-disubstituted-$\eta^5$-cycloheptadienyl products. This unique product may be formed from the proposed mechanism detailed in Scheme **63**. Protonation of the diene and hydrogen atom transfer reactions yield the cyclopentenyl intermediate **I**, as discussed previously. Coordination and insertion of the diphenylacetylene yield intermediate **II**. This intermediate then unexpectedly inserts into the far end of the coordinated alkene, generating bridged bicyclic complex **III**. Insertion of a second equivalent of alkyne into the cobalt-alkyl bond forms **IV**, which migrates onto the alkene carbon to form **V**. A β-alkyl elimination reaction relieves strain energy and forms the bicyclic skeleton of **VI**. Allylic activation of the hydrogen in the six-membered ring and reductive elimination of the resulting alkyl hydride form **VII**. Further β-hydride elimination and reinsertion form the final observed product, presumably driven by thermodynamic factors.

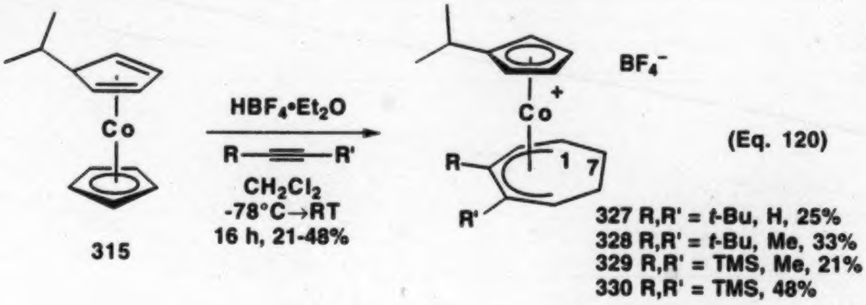
**Scheme 63**



No mechanistic work has been done to evaluate the pathway proposed and no other system has been observed to form structurally similar products, although the formation of bicyclic products has re-surfaced in the [5 + 2] cycloaddition reactions with acetylene.

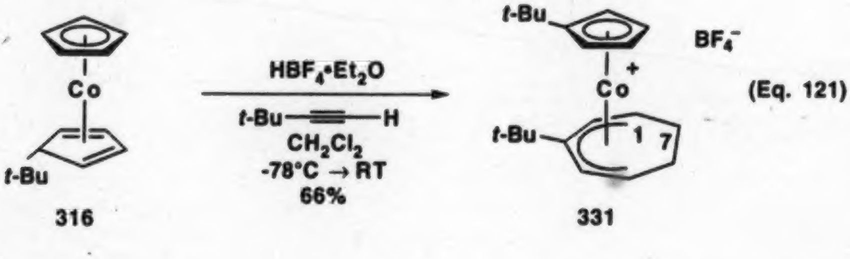
The methylcyclopentadienyl system **325** proved to be somewhat limiting with respect to the range of alkynes that cleanly undergo ring expansion. Electron poor alkynes, such as DMAD or ethyl tetrolate, for example, fail to yield tractable material other than a small amount of methylcobalticenium.

Given the limitations in the methyl substituted cyclopentadienyl complex that were observed, other alkyl-substituted cyclopentadienyl systems were evaluated. The *i*-Pr substituted system, CpCo(1-*i*-Pr-$C_5H_5$) **315** shows similar reactivity using alkyl- or silyl-substituted alkynes, but typically produces a large amount of cobalticenium byproduct. This system fails to give good yields of the seven-membered ring products **327**-**330** (Eq. **120**) and was quickly abandoned. In contrast, the reactivity of CpCo(1-*t*-Bu$C_5H_5$) (**316**) showed substantially more promise.

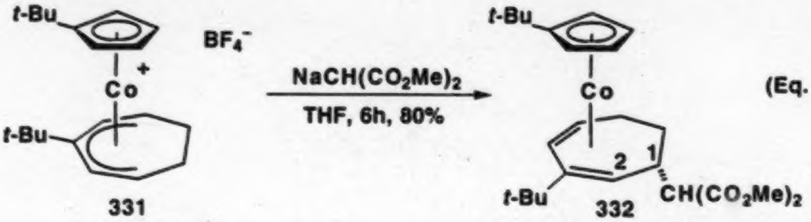

Co
315
HBF₄•Et₂O
R—≡—R'
CH₂Cl₂
-78°C→RT
16 h, 21-48%
Co +
BF₄⁻
R
R'
1
7
(Eq. 120)
327 R,R' = t-Bu, H, 25%
328 R,R' = t-Bu, Me, 33%
329 R,R' = TMS, Me, 21%
330 R,R' = TMS, 48%

### *D. Ring Opening Reactions of t-Butylcyclopentadienyl Cobalt Cyclopentadiene Ligands*

The reaction of ($C_5H_5$)Co(*t*-Bu$C_5H_5$) (**316**) with $HBF_4$•$Et_2O$ and *t*-butyl acetylene produces the seven-membered ring complex **331** in good yield (66%) (Eq. **121**). This seven-membered ring has a mirror plane of symmetry, which simplifies the signal multiplicity, removing some of the coupling constant information normally available in the spectrum. The 3-*t*-butylcycloheptadienyl ligand of complex **331** is readily identified by comparison of the spectroscopic data with those of the unsubstituted ($\eta^5$-$C_5Me_5$)Co(cycloheptadienyl)$^+$ system (Chapter 2, page 55).


Co
t-Bu
316
HBF₄•Et₂O
t-Bu—≡—H
CH₂Cl₂
-78°C → RT
66%
t-Bu
Co +
BF₄⁻
t-Bu
1
7
331
(Eq. 121)

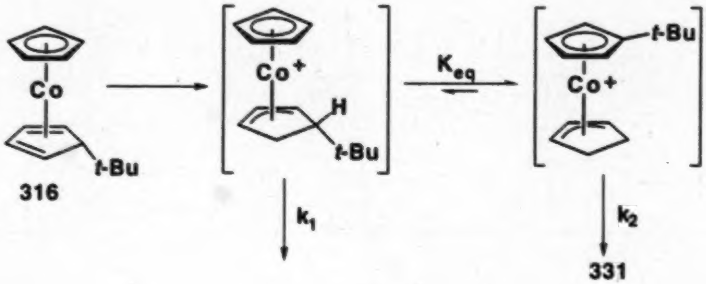
Addition of sodium dimethylmalonate to complex **331** provides the cobalt diene complex **332**, giving an additional confirmation of the structure of cycloheptadiene **331** (Eq. **122**). The disruption of symmetry in the adduct makes each position unique, and the full system can readily be assigned. The $^1$H NMR spectrum shows four separate signals for the *t*-butylcyclopentadienyl ligand, due to the asymmetry of the seven-membered ring.



(Eq. 122)

In contrast to the methylcyclopentadienyl system, only one $\eta^5$-cycloheptadienyl isomer is formed in the reaction of **316** with *t*-butylacetylene (Scheme **64**). This observation is consistent with the larger *t*-butyl group on a cyclopentenyl ligand inducing a greater steric barrier to alkyne insertion, (*i.e.*, a lower $k_1$), resulting in more selective reactions. A *t*-butyl group on the cyclopentadienyl ligand has minimal steric interaction with other atoms in the complex and thus this structure is expected to be favored in the equilibrium. Once again, the alkyne inserts in a regioselective manner, with the larger alkyne substituent eventually placed on the 3-position of the cycloheptadienyl product.

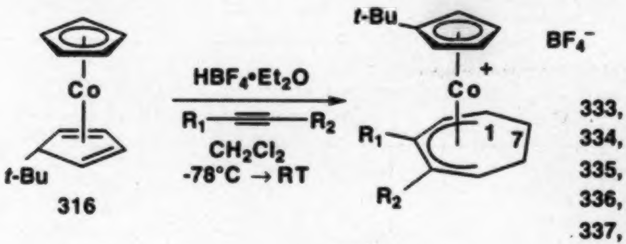
**Scheme 64**



Other differences between the $C_5H_4Me$ and $C_5H_4$-*t*-Bu systems are observed. In the reaction with diphenylacetylene, only one equivalent is incorporated into the product;

no evidence for double insertion is obtained (Eq. **123**). More importantly, a broader range of alkynes can be successfully inserted using the *t*-butyl template, including phenylacetylene and phenylpropyne, although the yields for the latter two remain low (*vide infra*). Other alkynes such as alkoxyalkynes and electron poor alkynes still fail to insert using this template.

The reactions of 4,4-dimethyl-2-pentyne, 1-(trimethylsilyl)propyne, bis(trimethylsilyl)acetylene (BTMSA), diphenylacetylene, and 2-butyne with the *t*-butylcyclopentadiene complex **316** all proceed in good to excellent yield to give ring expanded $\eta^5$-cycloheptadienyl complexes **333-337** (Eq. **123**). The $\eta^5$-cycloheptadienyl complexes **333-337** are isolated as red to orange powders after chromatography (silica gel, 5% methanol/dichloromethane) or crystallization from dichloromethane/diethyl ether. Comparative $^1$H NMR spectroscopic data for these complexes are presented in Table **10**. In particular, the reaction with BTMSA gives a particularly clean cycloheptadienyl product **335** after crystallization from chloroform/diethyl ether. This complex was further characterized by X-ray crystallography (Figure **15**).

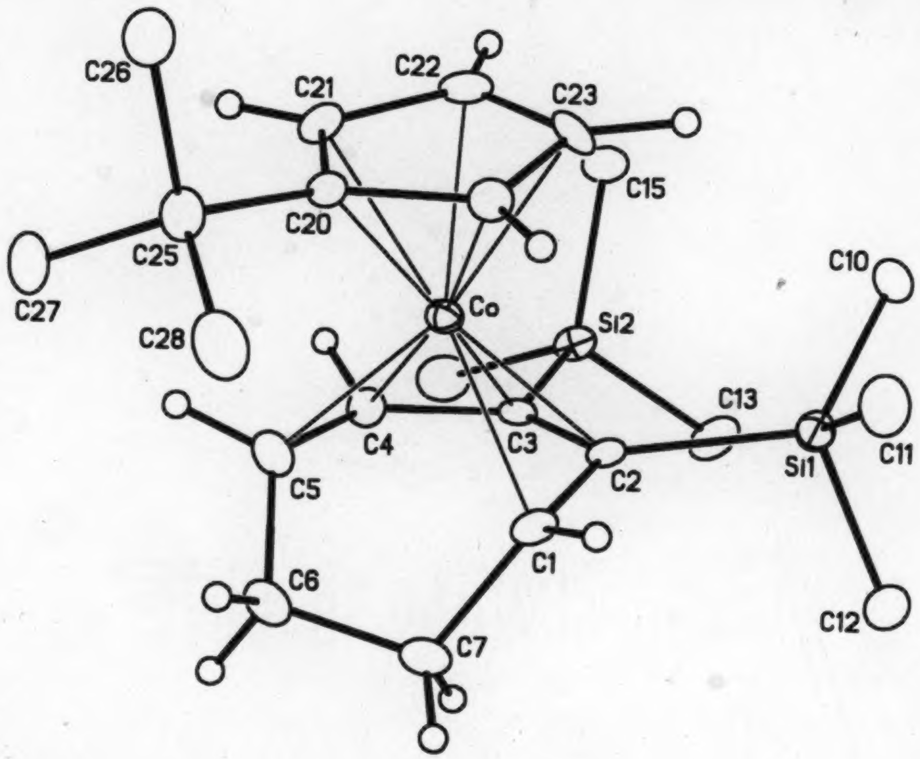


(Eq. 123)

**333, $R_1$ = *t*-Bu, $R_2$ = Me, 70%**
**334, $R_1$ = TMS, $R_2$ = Me, 72%**
**335, $R_1$ = $R_2$ = TMS, 79%**
**336, $R_1$ = $R_2$ = Ph, 70%**
**337, $R_1$ = $R_2$ = Me, 74%**

It is somewhat surprising that clean reactions occur with such large alkynes as the trimethylsilyl-substituted acetylenes. The large group on the alkyne appears to be beneficial for seven-membered ring formation in this system, as the reaction with 2-butyne proceeds in slightly lower yield than with most other alkynes. Because this observation contrasts with the results of ring opening reactions using the ($\eta^5$-$C_5Me_5$) template, an unspecified optimum steric profile may exist for C-C bond activation of the cyclopentenyl ligand.

**Figure 15**. ORTEP[115] for Complex **335** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS9716



Final Residuals: $R_1 = 0.0696$; $wR_2 = 0.1052$. Data obtained at -60°C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): Co-C1, 2.086(6); Co-C2, 2.041(5); Co-C3, 2.100(6); Co-C4, 2.022(6); Co-C5, 2.094(6); C1-C2, 1.425(7); C1-C7, 1.526(8); C2-C3, 1.438(8); C3-C4, 1.449(8); C4-C5, 1.409(8); C5-C6, 1.507(8); C6-C7, 1.492(8); Si1-C2, 1.915(6); Si1-C10, 1.870(6); Si1-C11, 1.857(7); Si1-C12, 1.871(6); Si2-C3, 1.935(6); Si2-C13, 1.863(6); Si2-C14, 1.858(7); Si2-C15, 1.858(6).

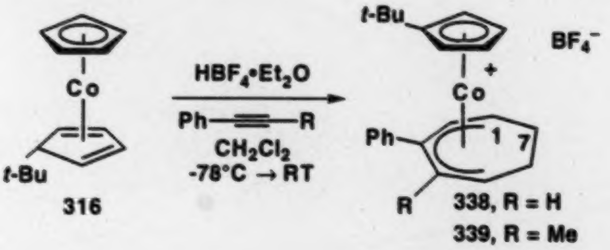
Selected Bond Angles (deg.): C1-C2-C3, 116.6(5); C2-C3-C4, 120.5(5); C3-C4-C5, 128.3(6); C4-C5-C6, 128.6(6); C5-C6-C7, 108.4(5); C1-C7-C6, 110.9(5); C2-Si1-C10, 116.8(3); C2-Si1-C11, 110.0(3); C2-Si1-C12, 104.4(3); C10-Si1-C11, 106.3(3); C10-Si1-C12, 111.4(3); C11-Si1-C12, 107.7(3); C3-Si2-C13, 110.3(3); C3-Si2-C14, 106.7(3); C3-Si2-C15, 113.7(3); C13-Si2-C14, 105.1(3); C13-Si2-C15, 112.8(3); C14-Si2-C15, 107.6(3); Si1-C2-C1, 114.5(4); Si1-C2-C3, 128.9(4); Si2-C3-C2, 127.8(4); Si2-C3-C4, 111.2(4).

**Table 10.** Comparative $^1$H NMR Spectroscopic Data For $t$-BuC$_5$H$_4$ $\eta^5$-Cycloheptadienyl Complexes

| | 331 | 333 | 334 | 335 | 336 | 337 |
|---|---|---|---|---|---|---|
| **H$_1$**<br>$J_{1\text{-}2}$ | 5.35 (m)<br>8.9 Hz | 5.49 (dddd)<br>9.5 Hz | 5.67 (dddd)<br>9.3 Hz | 5.94 (br d)<br>9.2 Hz | 5.85 (m)<br>a | 5.34 (m)<br>a |
| **H$_2$**<br>$J_{2\text{-}3}$ | 5.57 (d)<br>b | 5.33 (dd)<br>b | 5.22 (d)<br>b | 5.28 (d)<br>b | 5.85 (m)<br>b | 5.34 (m)<br>b |
| **H$_3$**<br>$J_{3\text{-}4}$ | b | b | b | b | b | b |
| **H$_4$**<br>$J_{4\text{-}5}$ | 5.57 (d)<br>8.9 Hz | b | b | b | b | b |
| **H$_5$**<br>$J_{5\text{-}6endo}$<br>$J_{5\text{-}6exo}$ | 5.35 (m)<br>a<br>a | 5.10 (dd)<br>8.4 Hz<br>4.8 Hz | 5.19 (dd)<br>8.2 Hz<br>5.0 Hz | 5.33 (dd)<br>8.2 Hz<br>5.2 Hz | 5.59 (dd)<br>8.4 Hz<br>4.7 Hz | 5.25 (dd)<br>8.1 Hz<br>4.4 Hz |
| **H$_{6endo}$**<br>$J_{6endo\text{-}6exo}$<br>$J_{6endo\text{-}7endo}$<br>$J_{6endo\text{-}7exo}$ | 2.4 (m)<br>a<br>a<br>a | 1.70 (m)<br>12.7 Hz<br>9 Hz<br>a | 1.80 (m)<br>11.7 Hz<br>9.7 Hz<br><2 Hz | 1.72 (br q)<br>12.3 Hz<br>8.5 Hz<br>0 Hz | 2.1 (m)$^c$<br>a<br>a<br>a | 1.95 (m)<br>13.8 Hz<br>9.6 Hz<br>1.9 Hz |
| **H$_{6exo}$**<br>$J_{6exo\text{-}7endo}$<br>$J_{6exo\text{-}7exo}$ | 1.15 (m)<br>a<br>a | 0.20 (dddd)<br>11.5 Hz<br>6.5 Hz | 0.23 (dddd)<br>11.7 Hz<br>5.8 Hz | 0.15 (tt)<br>9.5 Hz<br>6.0 Hz | 0.7 (m)<br>a<br>a<br>b | 0.45 (m)<br>10.2 Hz<br>6.3 Hz |
| **H$_{7endo}$**<br>$J_{7endo\text{-}7exo}$<br>$J_{7endo\text{-}1}$ | 2.4 (m)<br>a<br>a | 2.89 (dddd)<br>17.3 Hz<br>4 Hz | 2.99 (dddd)<br>17.6 Hz<br>3.5 Hz | 3.05 (dddd)<br>17.7 Hz<br>3.7 Hz | 3.15 (m)<br>a<br>a | 2.77 (dddd)<br>17.2 Hz<br>4.1 Hz |
| **H$_{7exo}$**<br>$J_{7exo\text{-}1}$ | 1.15 (m)<br>a | 1.93 (m)<br><2 Hz | 2.01 (br d)<br>3.5 Hz | 2.08 (dd)<br>2.7 Hz | 2.1 (m)$^c$<br>a | 1.76 (m)<br>a |

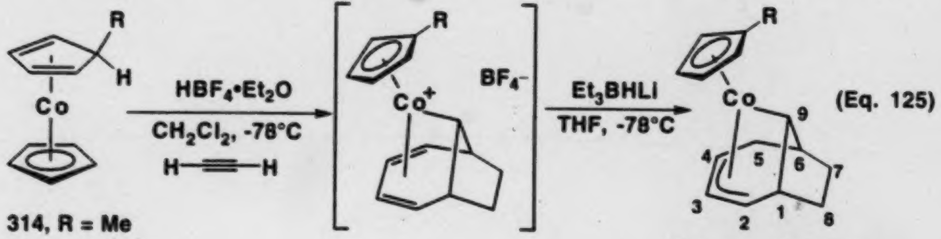
[a] Numerical value for the coupling constant was not obtained due to second order character or complexity of the signal. [b] Not applicable due to a non-hydrogen substituent. [c] Signals overlap.

The products obtained from the reaction of **316** with $HBF_4 \bullet Et_2O$ and phenylacetylene or 1-phenylpropyne in $CH_2Cl_2$ are readily identified as the 3-phenylcycloheptadienyl complexes **338** and **339** (Eq. **124**). These assignments are based primarily on the $^1H$ NMR spectrum of **338**, which shows a highly symmetrical product. This identification is obtained despite the inability to obtain the reaction product completely free from unidentified materials. The product **339** obtained from phenylpropyne incurs a similar problem with purification, but the $^1H$ NMR spectrum again shows signals that are consistent with the tentatively assigned structure. Because of significant impurities in the $^1H$ NMR spectra of these products, yields could not obtained accurately, but appear to be relatively low (*i.e.*, 5-15%). The impurities do not appear to be either cobalticenium products or other seven-membered rings as far as can be determined from the $^1H$ NMR spectrum.



(Eq. 124)

The reactions of acetylene with either methylcyclopentadiene complex **314** or *t*-butylcyclopentadiene complex **316** with $HBF_4 \bullet Et_2O$ in $CH_2Cl_2$ does not follow the general [5 + 2] reactivity pattern. The product obtained in either case is not stable enough to isolate directly without decomposition; however, treatment of the crude product with $Et_3BHLi$ provides the stable, although air-sensitive, cycloadducts **340** and **341** (Eq. **125**), as determined from extensive spectroscopic analysis. The furthest downfield signal in the $^1H$ NMR spectrum of the double insertion product **340** resonates at $\delta$ 4.54 ($H_4$). This signal is connected by a 7 Hz coupling constant to the central proton of the allyl ($H_3$), which resonates at 3.73 ppm. In turn, the $H_3$ signal is coupled to $\delta$ 4.25 ($H_2$, $J_{3\text{-}2} = 7$ Hz). These signals are shown by the HMQC spectrum to be attached to carbon atoms that resonate at 68.5 ($C_4$, ${}^1J_{CH}$ = 162 Hz), 83.5 ($C_3$, ${}^1J_{CH}$ = 156 Hz), and 53.4 ($C_2$, ${}^1J_{CH}$ = 162 Hz), respectively. Note that although the ${}^1$H NMR data is unusual for an allyl complex in that the central proton does not resonate furthest downfield and possibly



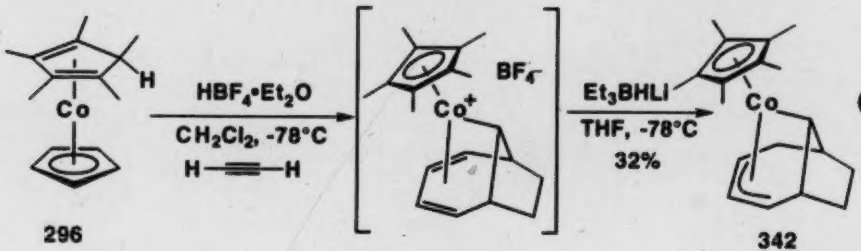
(Eq. 125)

**314, R = Me**
**316, R = *t*-Bu**

**340, R = Me, 72%**
**341, R = *t*-Bu, 81%**

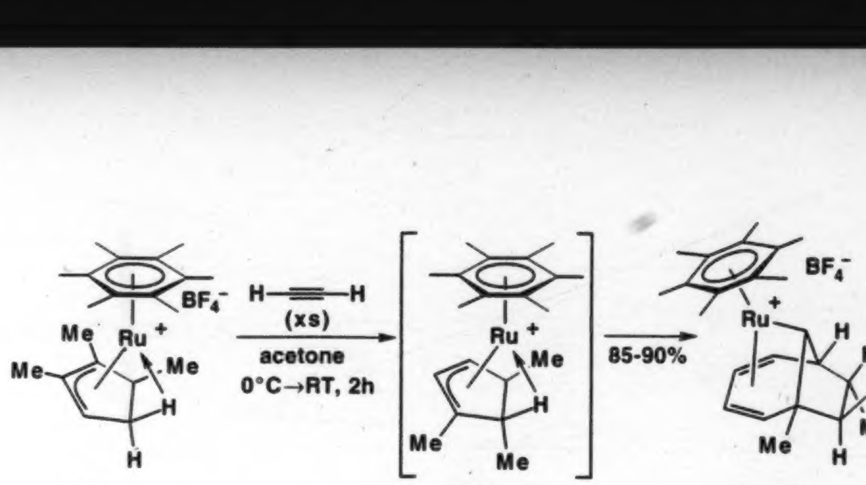
indicates a constrained geometry, the ${}^{13}$C NMR data is consistent and unremarkable. The δ 4.54 ($H_4$) signal is further correlated to two hydrogen atoms that resonate at δ 2.63 ($H_{5a}$) and δ 1.34 ($H_{5b}$) with coupling constants of 7 and 2 Hz, respectively. Furthermore, the two $H_5$ atoms are correlated with a mutual 16 Hz coupling constant. Both show coupling to a signal at δ 2.45 (m, $H_6$), with coupling constants of 11 and 2 Hz, respectively. The bridgehead $H_6$ atom resonates at 2.45 ppm, and shows correlations in the COSY spectrum to $H_{5a}$ and $H_{5b}$, as mentioned, but also to 1.42 ($H_9$) and the multiplet at 1.17 ($H_{7a/7b}$). Due to the multiplet character of both $H_6$ and $H_7$ signals, $J$ values could not be obtained. However, the $H_9$ proton has a well-resolved dd multiplicity pattern and decoupling experiments determine that $J_{6\text{-}9}$ = 7 Hz. The $H_9$ resonance also shows coupling to a signal at δ 2.80 ($H_1$, $J_{1\text{-}9}$ = 9 Hz). As the $H_1$ atom has one fewer correlations than the other bridgehead hydrogen ($H_6$), it resolves into a dddd multiplicity pattern, with additional couplings of 9 and 6 Hz to the $H_8$ protons. It is further adjacent to $H_2$ (4.25 ppm), as indicated by a coupling constant of 7 Hz. Data from the HMQC spectrum allow the assignment of several upfield carbon signals. The $C_5$ carbon is located at 40.1 ppm. The two bridgehead carbon atoms resonate at δ 48.0 ($C_6$) and δ 44.8 ($C_1$), while the two methylene carbons $C_7$ and $C_8$ resonate at 33.1 and 35.6 ppm, respectively. These values are relatively consistent with the number of substituents on each individual carbon atom. However, the remaining signal ($C_9$) is found at relatively high field: 8.7 ppm. Furthermore, the $^1J_{CH}$ value obtained for this carbon is 150 Hz, suggesting that the cobalt atom severely perturbs this carbon. The spectral data for **341** are very similar to those for **340**.

The double insertion reactivity pattern appears to be general for acetylene; the reaction of ($\eta^5$-$C_5H_5$)Co($\eta^4$-$C_5Me_5H$) (**296**) with $HBF_4 \cdot Et_2O$ and excess acetylene in $CH_2Cl_2$, followed by the reaction with $Et_3BHLi$ in THF, also yields a bicyclo[4.2.1]nonediyl complex **342** (Eq. **126**). However, it is unclear why the yield here is much lower than those obtained for the less substituted cyclopentadienyl complexes. When the reaction is carried out with only a slight excess (3 equiv) of acetylene, delivered by gas-tight syringe, the same product is isolated in a similar yield. This suggests that a concentration effect due to the large amounts of acetylene normally used in the [3 + 2 + 2] cycloaddition reactions is not a factor in this reaction. Further development of this interesting new reactivity pathway is warranted.



**296** **342** (Eq. 126)

Similar double insertion products have been observed in related ruthenium chemistry both in our research group and others.[120,237] The reactions of cyclopentenyl ruthenium complex **343** with acetylene, for example, ultimately yields the $\eta^1,\eta^4$-bicyclo[4.2.1]nonadienyl complex **345** (Eq. **127**). Apparently, the starting $\eta^3$-cyclopentenyl complex initially isomerizes to agostic intermediate **344**, which then inserts two acetylene molecules before cyclizing.

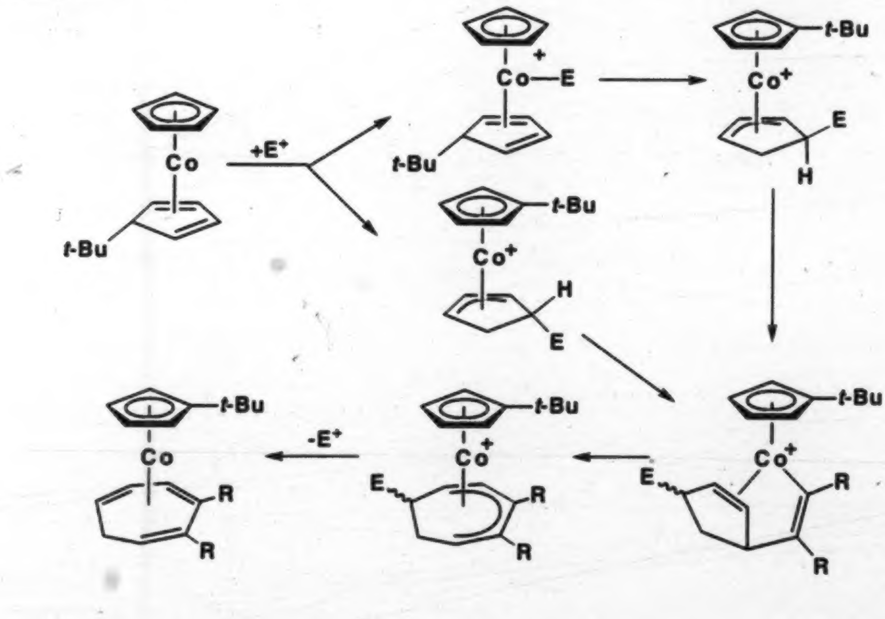

BF$_4^-$
Me
Ru$^+$
Me
Me
H
H
H—≡—H
(xs)
acetone
0°C→RT, 2h
Ru$^+$
Me
H
Me
Me
85-90%
BF$_4^-$
Ru$^+$
H
H
Me
Me
Me
H

**343** **344** **345**

(Eq. 127)

The reaction of ($\eta^5$-$C_5H_5$)Co($\eta^4$-*t*-Bu$C_5H_5$) (**316**) with $HBF_4$•$Et_2O$ and alkyne showed enough tolerance for alkyne substituents that it was selected as a model system for testing the reactivity of other electrophiles, in an attempt to introduce additional substituents and functionality into the seven-membered ring. Strong acids and non-coordinating anions work efficiently; thus, we hoped that other strong electrophiles would react with the cobalt diene to form a cyclopentenyl system. The use of alternative electrophiles could also be an important step in the development of a catalytic reaction (Scheme **65**), where loss of the electrophile after ring formation could generate a

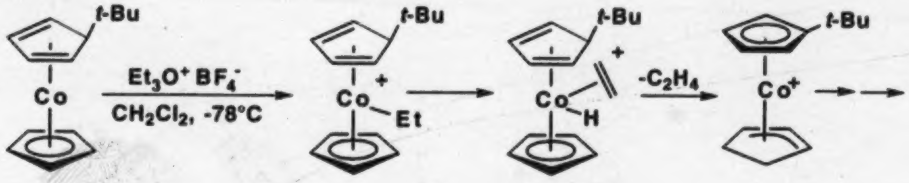
**Scheme 65**


Co
*t*-Bu
+E$^+$
Co—E
+
*t*-Bu
Co$^+$
*t*-Bu
E
H
*t*-Bu
Co$^+$
H
E
*t*-Bu
Co$^+$
E
R
R
*t*-Bu
Co$^+$
E
R
R
-E$^+$
*t*-Bu
Co
R
R

cycloheptatriene complex, which should be much easier to remove from the metal by exchange than the formally anionic cycloheptadienyl ligand (Scheme **65**).

However, the treatment of the *t*-butylcyclopentadiene complex **316** with various electrophiles in the presence of an alkyne gave disappointing results. Trimethyloxonium tetrafluoroborate fails to induce any reaction at all. Triethyloxonium, in contrast, generates small amounts of an $\eta^5$-cycloheptadienyl product upon reaction with **316** and *t*-butylacetylene. However, no incorporation of the ethyl group is seen in the $^1$H NMR spectrum. One possible rationale for this observation is that the ethyl group is delivered directly to the metal to form an ethyl cyclopentadiene complex (Scheme **66**). β-Hydrogen elimination from the ethyl group can generate a metal hydride, which transfers to the ring, and ethylene, which presumably is lost. The cyclopentenyl complex then reacts with alkyne to form the same cycloheptadienyl product expected from protonation.

**Scheme 66**



Trimethylsilyl triflate was also tested as an initiator, but met with very limited success. By TLC analysis, a very small amount of seven-membered ring is formed in the reaction between complex **316**, TMSOTf, and excess alkyne in $CH_2Cl_2$. However, a substantial quantity of cobalticenium complex is also formed, suggesting that this particular eletrophile favors the elimination to form cobalticenium complexes.

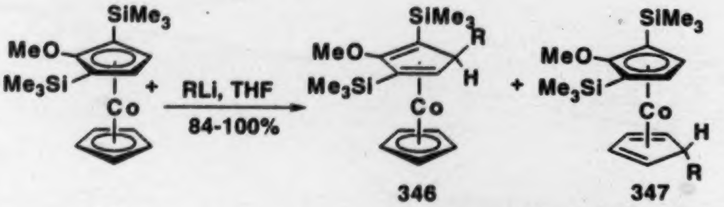
## *E. Ring Opening Reactions of Disubstituted Cyclopentadienyl Cobalt Cyclopentadiene Ligands*

Although the *t*-butylcyclopentadienyl template shows a reasonable tolerance towards substituents on the alkyne, it is also important for the development of a synthetically useful reaction to introduce alkyl or functional substituents onto the cyclopentadiene ligand. The competitive ring opening observed in the reaction between methylcyclopentadiene complex **314** and *t*-butylacetylene also raises fundamental questions about the factors that govern the equilibrium between the two cyclopentenyl systems. Thus, a brief study of 1,1'-disubstituted cobaltocene ring systems was undertaken.

Surprisingly few methods have been used for the synthesis of unsymmetrically disubstituted cobaltocene or cobalticenium compounds. Symmetrical cobaltocene complexes are readily made from $CoBr_2$ and two equivalents of a cyclopentadienyllithium reagent, but this route is not easily extended to unsymmetrical complexes. The cobalt complex $[(\eta^5\text{-}C_5Me_5)CoCl]_2$ is known and stable,[106] providing an easy route to substituted cobaltocene complexes $(\eta^5\text{-}C_5Me_5)Co(C_5H_nR_{5\text{-}n})$ via reaction with $Na(C_5H_nR_{5\text{-}n})$. The analogous $[(\eta^5\text{-}C_5H_5)CoCl]_2$ dimer is unfortunately not isolable, although it has been reported as a reactive intermediate.[238] Attempted reactions of this intermediate with other cyclopentadienyl salts, however, failed to give pure unsymmetrical cobalticenium salts. This intermediate is highly unstable and easily disproportionates to $(\eta^5\text{-}C_5H_5)_2Co$ and $CoBr_2$, which renders it unsuitable for the synthesis of systems with mixed cyclopentadienyl ligands. Mono-substituted cyclopentadienyl salts appear to induce similar problems in this synthetic approach.

A related strategy is ligand exchange of a substituted cyclopentadiene such as methylcyclopentadiene into a labile cyclopentadienyl cobalt complex, *i.e.*, (1-alkyl-$C_5H_4)Co(C_2H_4)_2$. Although we did not evaluate this strategy experimentally, there appear to be several drawbacks to this method. The required (alkyl-$C_5H_4$)Co($C_2H_4$)$_2$ complexes are not easily synthesized, demanding the use of potassium sand to reduce the starting 1,1'-dialkylcobalticenium complex. The other hurdle is the exchange itself; in the $C_5Me_5$ chemistry, the exchange reaction does not proceed well thermally and photolyic reactions generate a mixture of products.

There have been several reports of reactions of substituted cobalticenium complexes with nucleophiles. Generally, addition of the nucleophile occurs at both rings, giving a mixture of products. Malkov has shown the that addition of hydride to various 1,1'-disubstituted cobalticenium salts generates mixtures of isomers.[235] Vollhardt has undertaken a study of various steric and electronic effects on the addition of alkyllithium reagents to substituted cobalticenium complexes (Eq. **128**).[235] Except in situations where a large steric barrier to the addition exists, mixtures of isomeric addition products (**346** and **347**) were again obtained.

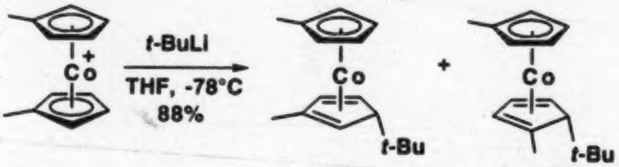


(Eq. 128)

| R | 346 | : 347 |
|---|---|---|
| t-Bu | 0 | 100 |
| Me | 29 | 71 |
| H | 75 | 25 |

To successfully utilize unsymmetrical ($\eta^5$-$C_5H_4R$)Co($\eta^4$-$C_5H_5R'$) complexes in the [5 + 2] ring expansion reactions, two initial criteria are suggested. The starting cyclopentadiene complex should preferentially exist as only one isomer and, in order to reduce the possible permutations of ring opening, one ring should be substantially more sterically crowded than the other. Thus, one simple target would have a methyl group on one ring and two larger groups on the other. A simple approach to a such a disubstituted complex is to add *t*-BuLi to 1,1'-dimethylcobalticenium cation, in the hope that the addition of the large *t*-Bu group would generate only one adduct, presumably with the *t*-butyl group located in a 1,3-relationship with the methyl substituent. By starting with a symmetrical cobalticenium complex, it does not matter which ring undergoes nucleophilic addition.

Unfortunately, when 1,1'-dimethylcobalticenium hexafluorophosphate reacts with *t*-butyllithium (THF, -78°C), a deep red oil is obtained in 88% yield which proved to be a mixture of two isomers (**348A** and **348B**) in approximately a 2:1 ratio (Eq. **129**). This mixture is assumed to be the 1,2- and 1,3-disubstituted cyclopentadiene complexes, but due to a number of overlapping signals in the $^1$H NMR spectrum, it is difficult to determine which isomer is the major product. However, the ring expanded products obtained from the reaction of these complexes indicate that the major isomer is the 1,3-disubstituted complex **348A**, as expected if steric interactions are minimized.



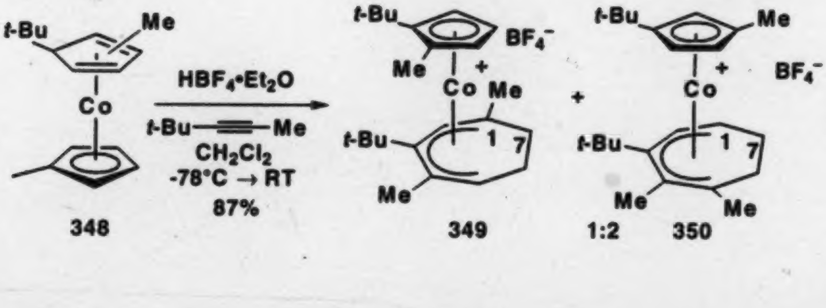
**348A** 2:1 **348B**

(Eq. 129)

The reactions of this mixture of cyclopentadiene isomers with $HBF_4 \bullet Et_2O$ in the presence of alkyne give high yields of cycloheptadienyl complexes resulting from ring opening of the less substituted methylcyclopentadiene ligand but the products are generally mixtures of 1,2- and 1,3-disubstituted cyclopentadienyl complexes. On occasion, additional minor products are seen. The exact composition of the product mixture is often difficult to determine, although most reactions appear to give one major and one minor product isomer. In such cases, careful purification by either recrystallization or flash chromatography yields the major isomer as a material pure enough for full spectroscopic analysis. Yields given are for the mixture of all seven-membered ring products after crude separation of the other impurities by flash chromatography. Individual products are obtained in low yields, as typically only a small amount of an individual isomer is recovered in a pure state.

This particular system also exhibits several unique properties in seven-membered ring production, so despite its shortcomings, further exploration and determination of its reactivity was undertaken. This template shows a much wider tolerance of functional groups on the alkyne. The reaction with electron deficient alkynes such as ethyl 2-butynoate proceeds to form seven-membered rings, in contrast to any template previously tested. Also in contrast to the unsubstituted cyclopentenyl systems, ring expansion leads to the formation of isomeric substitution patterns on the cycloheptadienyl ligand. Both 1,3,4- and 3,4,5-trisubstituted cycloheptadienyl complexes have been isolated from reactions using this template, but the 1,3,4-cycloheptadienyl isomer is generally predominant.

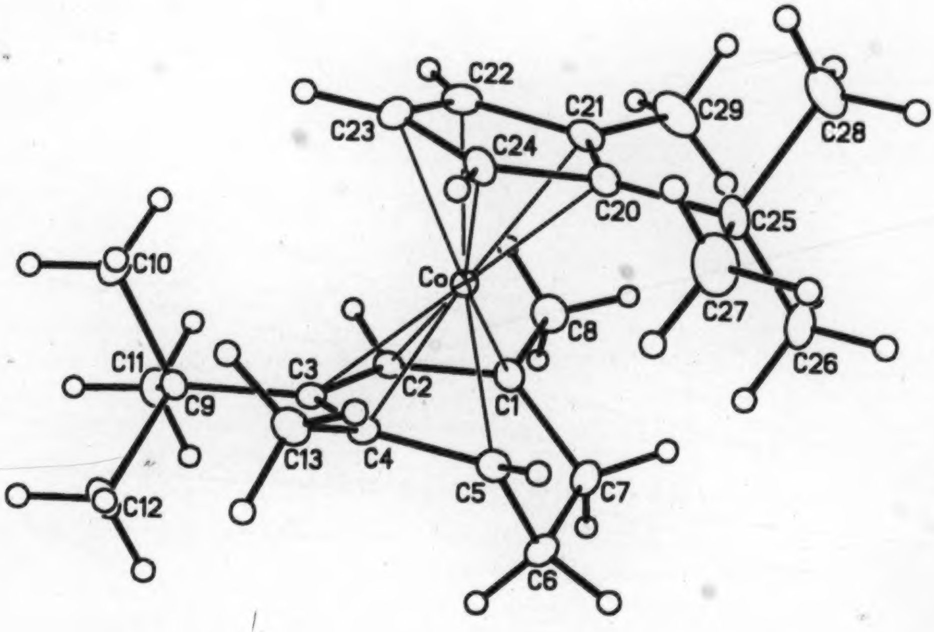
The reaction of the mixture of regioisomeric complexes $(\eta^5\text{-MeC}_5\text{H}_4)\text{Co}(\eta^4\text{-}t\text{-Bu-Me-C}_5\text{H}_3)$ **248A** and **248B** with 4,4-dimethyl-2-pentyne is illustrative (Eq. **130**). The crude mixture of cycloheptadienyl compounds, formed in 87% yield, contains only two compounds, in an approximately 2:1 ratio. The minor isomer could be partially extracted into ethyl acetate without contamination and was crystallized to give a pure compound, which yielded X-ray quality crystals upon recrystallization. The major isomer proved to be difficult to purify, although careful column chromatography (silica gel, 1-2% methanol/dichloromethane) provides material pure enough for complete spectroscopic analysis. The minor isomer was identified as $[(\eta^5\text{-1-}t\text{-Bu-2-Me-C}_5\text{H}_3)\text{Co}(\eta^5\text{-1,4-Me}_2\text{-3-}t\text{-BuC}_7\text{H}_6)]^+ \text{BF}_4^-$ **349** by X-ray crystallography (Figure **16**). The major isomer, which



348 349 1:2 350

(Eq. 130)

**Figure 16**. ORTEP[115] for Complex **349** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS9807



Final Residuals: $R_1 = 0.0535$; $wR_2 = 0.1126$. Data obtained at -60°C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å):
Co-C1, 2.157(4); Co-C2, 2.027(4); Co-C3, 2.134(4); Co-C4, 2.039(4); Co-C5, 2.093(4); C1-C2, 1.419(6); C1-C7, 1.499(6); C1-C8, 1.516(6); C2-C3, 1.433(6); C3-C4, 1.439(6); C3-C9, 1.543(6); C4-C5, 1.418(6); C4-C13, 1.513(6); C5-C6, 1.511(6); C6-C7, 1.502(6); C9-C10, 1.527(6); C9-C11, 1.540(6); C9-C12, 1.537(6).

Selected Bond Angles (deg.):
C2-C1-C7, 127.1(4); C2-C1-C8, 114.7(4); C7-C1-C8, 111.6(4); C1-C2-C3, 131.7(4); C2-C3-C4, 119.3(4); C2-C3-C9, 116.9(4); C4-C3-C9, 123.7(4); C3-C4-C5, 117.4(4); C3-C4-C13, 124.4(4); C5-C4-C13, 118.1(4); C4-C5-C6, 122.2(4); C5-C6-C7, 110.7(4); C1-C7-C6, 110.7(4); C10-C9-C11, 106.6(4); C10-C9-C12, 110.4(4); C11-C9-C12, 106.3(4).

was not amenable to crystallization, was identified spectroscopically as [($\eta^5$-1-*t*-Bu-3-Me-$C_5H_3$)Co($\eta^5$-4,5-$Me_2$-3-*t*-Bu$C_7H_6$)]$^+$ $BF_4^-$ **350**. Each isomer of the starting cyclopentadiene mixture therefore leads to the formation of a different cycloheptadienyl product.

It is immediately apparent from the respective $^1$H NMR spectra that these isomers not only differ in the cycloheptadienyl ligand substitution, but also have dissimilar cyclopentadienyl rings. Using these cycloheptadienyl complexes as a basis for comparison, the products from other alkyne insertion reactions can be assigned specific substitution patterns in the cyclopentadienyl rings. In the $^1$H NMR spectra, the signals for the two ring isomers differ only slightly (Table **11**). The values of the coupling constants are not diagnostic, as W- type and vicinal coupling constants in cyclopentadienyl rings are of the same magnitude (2-3 Hz). Some signals also have nearly identical chemical shifts, in particular the most downfield signal. However, the two remaining protons on the cyclopentadienyl ring appear to be characteristic of the individual substitution pattern. In particular, in the $^1$H NMR spectrum, the most upfield signal of the cyclopentadienyl ring resonates at approximately $\delta$ 4.77 for the 1,3-isomer (**350**) and at higher field (about 4.37 ppm) for the 1,2-isomer (**349**). The final signal also appears to be about 0.4 ppm more shielded in the 1,2-isomer of the cyclopentadienyl ligand. Although the methyl group of the ligand does not appear to show any characteristic shift for either isomer, the *t*-butyl group resonance can be quite diagnostic. The signal for the *t*-butyl group in the 1,3-isomer resonates at $\delta$ 1.18; in the 1,2-complex, the resonance appears further downfield.

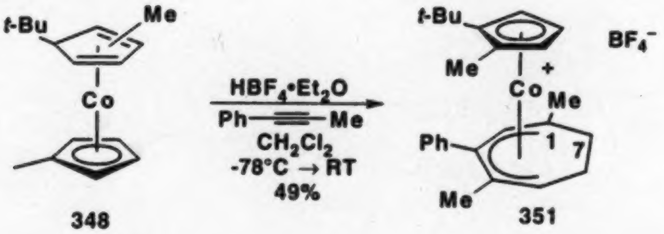
**Table 11.** Comparison of $^1$H NMR Spectra for 1,2 and 1,3 Disubstituted Cyclopentadienyl Ligands.

| **1,3 isomers** | CH | CH | CH | Me | *t*-Bu |
|---|---|---|---|---|---|
| **350** | 5.27 (t) | 5.16 (t) | 4.87 (t) | 2.47 | 1.14 |
| **352** | 5.31 (t) | 5.00 (t) | 4.68 (dd) | 2.47 | 1.12 |
| **353** | 5.37 (m) | 5.37 (m) | 4.60 (t) | 1.87 | 1.23 |
| **354** | 5.37 (s) | 5.09 (s) | 3.47 (s)[a] | 2.34 | 1.16 |
| **355** | 5.50 (t) | 5.41 (t) | 4.58 (t) | 1.87/1.85[b] | 1.27 |
| **356** | 5.68 (br s) | 5.37 (t) | 4.99 (t) | 2.55 | 1.18 |
| **357** | 5.82 (t) | 4.91 (t)[a] | 4.88 (t) | 2.40 | 1.17 |
| average | 5.47±0.21 | 5.23±0.17 | 4.77±0.17 | 2.28±0.29 | 1.18±0.05 |
| **1,2 isomers** | | | | | |
| **349** | 5.11 (t) | 4.91 (t) | 4.37 (t) | 2.25 | 1.64/1.42[b] |
| **351** | 5.39 (t) | 4.78 (t) | 4.36 (t) | 2.20 | 1.42 |
| average | 5.25±0.20 | 4.85±0.09 | 4.37±0.01 | | |

[a] Value not included for average calculations. [b] More than one *t*-butyl group is present and specific assignments could not be made. Where resolved, all coupling constants have a measured value of 2-3 Hz.

Most of the isolated complexes thus appear to have a 1,3-substitution pattern in the cyclopentadienyl ring, supporting the assignment that it is the dominant isomer formed in the starting diene complex. From a steric viewpoint, it is expected that the large *t*-BuLi reagent would favor the less hindered approach to the cobalticenium ring, preferentially generating the 1,3 isomer. It is possible that the observed 2:1 ratio could be influenced by changing the reaction conditions, for example, by using lower reaction temperatures. It is also conceivable that using a solvent with a lower polarity than THF could change the product ratio by encouraging larger aggregate formation and generating a larger steric barrier to formation of the 1,2-isomer. One final approach could be the use of TMSLi instead of *t*-BuLi to generate the initial cyclopentadiene complex. The TMS group could be hydrolyzed after the alkyne insertion reaction, thus eliminating the cyclopentadienyl ring as a source of additional isomers, but retaining the large steric presence required in this process. None of these approaches have as yet been evaluated experimentally.

The only other product characterized as a 1,2-cyclopentadienyl ring system is the major compound obtained from the reaction of **348** with 1-phenylpropyne (Eq. **131**). The total yield for this reaction is not high, but this template is unique in providing workable amounts of a cycloheptadienyl product using this alkyne. Complex **351** is characterized as the 1,3,4-trisubstituted cycloheptadienyl ligand based on the singlet at δ 5.52 in the $^1$H NMR spectrum, indicative of the isolated $H_2$ signal. The other signal on the pentadienyl fragment, due to $H_5$, resonates at 5.10 ppm and shows two couplings to mutually coupled hydrogen atoms $H_{6endo}$ ($J$ = 8.1 Hz) and $H_{6exo}$ ($J$ = 4.4 Hz), which resonate at δ 1.97 and 1.42, respectively.



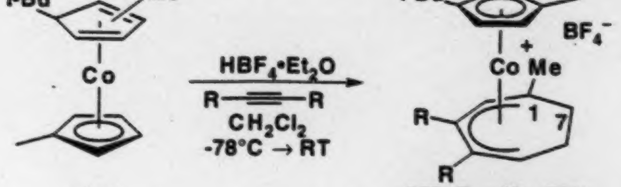
(Eq. 131)

The reactions of the starting complex **348** with $HBF_4$•$Et_2O$ and the disubstituted alkynes 2-butyne, cyclooctyne, and diphenylacetylene in $CH_2Cl_2$ (Eq. **132**) all give similar results, where only one major compound is observed in the $^1$H NMR spectrum of the crude product. Column chromatography (silica gel, 5% methanol/dichloromethane) effects the isolation and purification of the major 1,3,4-trisubstituted $\eta^5$-cycloheptadienyl complexes **352-354**, characterized unambiguously by the full array of NMR spectroscopic techniques. The crude yield is reported for complexes **352** and **353**; thus, small amounts of other isomers are still present, giving a higher yield than expected based on the 2:1 ratio of starting isomers, although an isomerization process may be active. Comparative $^1$H NMR data for this substitution pattern are presented in Table **12**.

**Table 12**. Comparative $^1$H NMR Spectrocopic Data for 1,3,4 Substituted Cycloheptadienyl Complexes

| | 349 | 351 | 352 | 353 | 354 |
|---|---|---|---|---|---|
| **$H_1$**<br>$J_{1\text{-}2}$ | b | b | b | b | b |
| **$H_2$**<br>$J_{2\text{-}3}$ | 5.30 (s)<br>b | 5.52 (s)<br>b | 5.34 (s)<br>b | 5.68 (s)<br>b | 5.14 (s)<br>b |
| **$H_3$**<br>$J_{3\text{-}4}$ | b | b | b | b | b |
| **$H_4$**<br>$J_{4\text{-}5}$ | b | b | b | b | b |
| **$H_5$**<br>$J_{5\text{-}6endo}$<br>$J_{5\text{-}6exo}$ | 4.80 (dd)<br>8.3 Hz<br>4.6 Hz | 5.10 (dd)<br>8.1 Hz<br>4.4 Hz | 4.96 (dd)<br>7.3 Hz<br>4.1 Hz | 5.41 (dd)<br>8.1 Hz<br>4.5 Hz | 4.92 (dd)<br>7.7 Hz<br>4.3 Hz |
| **$H_{6endo}$**<br>$J_{6endo\text{-}6exo}$<br>$J_{6endo\text{-}7endo}$<br>$J_{6endo\text{-}7exo}$ | 1.65 (m)<br>12.5 Hz<br>9.0 Hz<br>a | 1.97 (m)<br>13.9 Hz<br>9.2 Hz<br>a | 2.12 (m)<br>15 Hz<br>10 Hz<br>4 Hz | 2.10 (m)<br>a<br>9.6 Hz<br>a | 1.63 (m)[c]<br>14.3 Hz<br>9.1 Hz<br>a |
| **$H_{6exo}$**<br>$J_{6exo\text{-}7endo}$<br>$J_{6exo\text{-}7exo}$ | 0.20 (m)<br>10.8 Hz<br>9.7 Hz | 1.42 (m)<br>9.2 Hz<br>a | 0.70 (m)<br>8 Hz<br>6 Hz | 0.57 (m)<br>9.6 Hz<br>a | 0.46 (m)<br>9.1 Hz<br>5.6 Hz |
| **$H_{7endo}$**<br>$J_{7endo\text{-}7exo}$<br>$J_{7endo\text{-}1}$ | 2.57 (ddd)<br>17.7 Hz<br>b | 2.65 (m)<br>18.9 Hz<br>b | 2.39 (ddd)<br>16.2 Hz<br>b | 2.84 (ddd)<br>18.3 Hz<br>b | 2.62 (ddd)<br>16.7 Hz<br>b |
| **$H_{7exo}$**<br>$J_{7exo\text{-}1}$ | 1.75 (m)<br>b | 1.85 (m)<br>b | 1.44 (ddd)<br>b | 2.10 (m)<br>b | 2.05[c] (m)<br>b |

[a] Numerical value for the coupling constant was not obtained due to second order character or complexity of the signal. [b] Not applicable due to a non-hydrogen substituent. [c] Signal is obscured, chemical shift is estimated from the COSY spectrum.

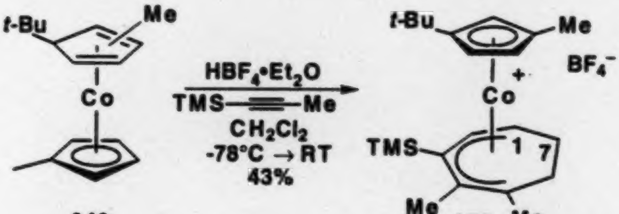


348

352, R = Me, 78%
353, R = Ph, 77%
354, R = -(CH$_2$)$_6$-, 43%

(Eq. 132)

Another significant result is obtained from the reaction of cyclopentadiene complex **348** with HBF$_4$•Et$_2$O and trimethylsilylpropyne (Eq. **133**). Crystallization provides one product isomer, isolated in 43% yield, and characterized as the 3,4,5-trisubstituted cycloheptadienyl complex **355**. It is unusual for such complexes to crystallize directly, as the large number of alkyl groups engender high solubility. The $^1$H NMR spectrum of the mother liquor from the crystallization did not appear to contain additional cycloheptadienyl isomers: only several unidentified minor compounds were observed. The trimethylsilyl group is easily recognized by the large singlet at 0.55 ppm. The seven-membered ring has several identifying features, especially the upfield signal at 0.03 ppm, characteristic of $H_{6exo}$. The 3,4,5-cycloheptadienyl ligand substitution pattern is confirmed by downfield signals at δ 4.97 (d, $J$ = 9.3 Hz, $H_2$) and δ 4.88 (m, $H_1$), which share a mutual 9 Hz coupling constant. The remaining structural features are fully supported by COSY, HMQC, and HMBC spectra. Comparative spectroscopic data for this substitution pattern is presented in Table **13**.



348

355

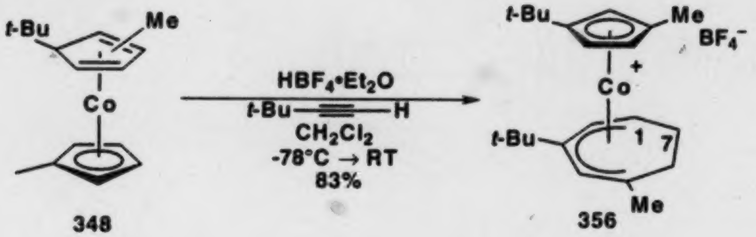
(Eq. 133)

**Table 13**. Comparative $^1H$ NMR Spectroscopic Data for 3,4,5-Substituted Cycloheptadienyl Complexes

| | **350** | **355** | **356** | **357** |
|---|---|---|---|---|
| **$H_1$** | 5.00 (m) | 4.88 (dq) | 4.64 (m) | 4.97 (dq) |
| $J_{1\text{-}2}$ | 8.0 Hz | 9.3 Hz | 8.5 Hz | 9.6 Hz |
| **$H_2$** | 4.89 (d) | 4.97 (d) | 5.28 (d) | 5.49 (dd) |
| $J_{2\text{-}3}$ | b | b | b | b |
| **$H_3$** | b | b | b | b |
| $J_{3\text{-}4}$ | | | | |
| **$H_4$** | b | b | 5.68 (s) | b |
| $J_{4\text{-}5}$ | | | b | |
| **$H_5$** | b | b | b | b |
| $J_{5\text{-}6endo}$ | | | | |
| $J_{5\text{-}6exo}$ | | | | |
| **$H_{6endo}$** | 1.05 (ddd) | 1.21 (ddd) | 1.90 (m) | 1.43 (m) |
| $J_{6endo\text{-}6exo}$ | 11.5 Hz | 11.4 Hz | 13.8 Hz | 12.3 Hz |
| $J_{6endo\text{-}7endo}$ | 6.6 Hz | 6.9 Hz | 8.8 Hz | 7.2 Hz |
| $J_{6endo\text{-}7exo}$ | 1.9 Hz | ca. 0 Hz | 3.4 Hz | a |
| **$H_{6exo}$** | -0.19 (ddd) | 0.03 (ddd) | 0.73 (ddd) | 0.10 (ddd) |
| $J_{6exo\text{-}7endo}$ | 12.8 Hz | 12.7 Hz | 8.8 Hz | 12.3 Hz |
| $J_{6exo\text{-}7exo}$ | 4.6 Hz | 4.6 Hz | 6.0 Hz | 4.6 Hz |
| **$H_{7endo}$** | 3.03 (dddd) | 3.14 (dddd) | 2.85 (dddd) | 3.32 (dddd) |
| $J_{7endo\text{-}7exo}$ | 17.7 Hz | 17.7 Hz | 16.3 Hz | 18.0 Hz |
| $J_{7endo\text{-}1}$ | 2.4 Hz | 2.7 Hz | 4.1 Hz | 3.3 Hz |
| **$H_{7exo}$** | 2.31 (m) | 2.31 (ddd) | 1.65 (m) | 2.29 (ddd) |
| $J_{7exo\text{-}1}$ | a | 2.7 Hz | 4.1 Hz | 3.3 Hz |

[a] Numerical value for the coupling constant was not obtained due to second order character or complexity of the signal. [b] Not applicable due to a non-hydrogen substituent.

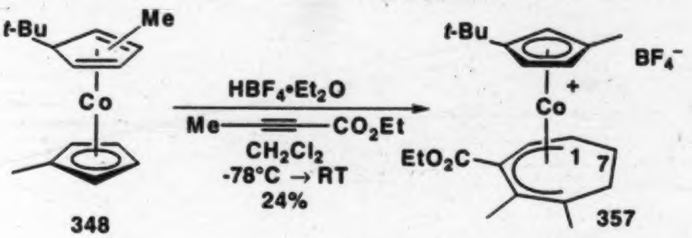
In order to generate a single seven-membered ring isomer, the reaction of *t*-butylacetylene with the starting cyclopentadiene **348** was investigated (Eq. **134**). Since the cyclopentenyl complex always appears to insert into the unsubstituted side of the alkyne, only one cycloheptadienyl isomer should be generated. Thus, cycloheptadienyl complex **356** was obtained in very good yield as the only major product when cyclopentadiene **348** reacts with $HBF_4•Et_2O$ and *t*-butylacetylene in $CH_2Cl_2$. Presumably, the use of the corresponding deuterated alkyne in this reaction would yield information on the orientation of this insertion, although this study has not yet been undertaken.



(Eq. 134)

The orange $\eta^5$-cycloheptadienyl complex **356** was isolated through column chromatography and is consistent with the formulation of a 1,3-disubstituted cyclopentadienyl complex (Table **11**). Although a very small amount of another product is observed in the $^1H$ NMR spectrum of the crude product, an insufficient amount was formed to conclusively identify. This suggests that the 1,2-cyclopentadienyl isomer decomposes, forms insignificant amounts of minor products, or potentially isomerizes to the 1,3 complex. In order to evaluate the potential isomerization, pure 1,2-*t*-butyl-methylcyclopentadiene complex **348B** will have to be synthesized and subjected to the reaction conditions to ascertain if any 1,3-isomer is produced. The high yield of the reaction may also be attributed to small amounts of unidentified isomeric complexes present in the crude product.

This template also demonstrates a rare but marginal tolerance for electron withdrawing groups on the alkyne, as a seven-membered ring product is obtained from the reaction of **348** with $HBF_4 \bullet Et_2O$ and ethyl 2-butynoate, producing a low yield (24%) of a characteristic red oil (Eq. **135**). Although two isomeric cycloheptadiene complexes may be formed, only one isomer (**357**) could be conclusively identified in the crude $^1H$ NMR spectrum. This isomer could be isolated and purified to some extent by column chromatography (silica gel, 2% methanol/dichloromethane). The 3,4,5-cycloheptadienyl ligand is readily identified by the two coupled downfield signals in the $^1H$ NMR spectrum at 5.49 and 4.97 ppm. Other spectral data is consistent with this structure, and the band at 1725 $cm^{-1}$ in the IR spectrum clearly demonstrates the presence of the ester.

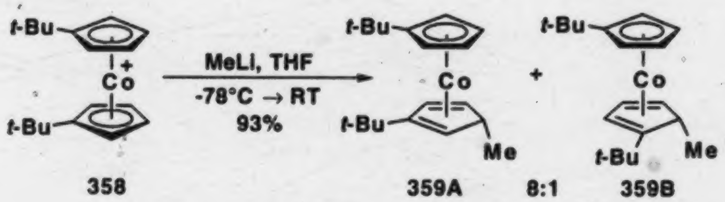


(Eq. 135)

Given the isomeric mixture of cyclopentadiene starting complexes, it is more than a little strange that, in most cases, only one major reaction product is isolated. Given the 2:1 mixture of regioisomers in the starting cyclopentadiene complexes **348**, it might be expected that four products would form in a 2:2:1:1 ratio: the 1,3-isomer of the *t*-butylmethylcyclopentadiene ring producing a 3,4,5- and a 1,3,4-cycloheptadienyl complex and similarly, the 1,2-substituted cyclopentadienyl isomer yielding two seven-membered ring isomers. Based on other systems, products arising from insertion of the alkyne into the more substituted cyclopentadienyl ring were not anticipated, although such reactions cannot be dismissed conclusively. Thus, each isomer apparently favors a different intermediate and transition state for the coordination and insertion of the alkyne. One regioisomer in the starting diene complex selectively reacts to form a particular cycloheptadienyl isomer. The other initial cyclopentadiene regioisomer either does not react to form a seven-membered ring, or reacts to form several different products, or rearranges under the reaction conditions to give the dominant regioisomer prior to reaction with alkyne. This is difficult to ascertain conclusively, as it has proven to be prohibitively difficult to separate and characterize minor components.

This particular cyclopentadiene system was also found to insert several other alkynes upon protonation. Reaction of this template with $HBF_4{\bullet}Et_2O$ and bis(trimethylsilyl)acetylene gives a high (83%) yield of seven-membered ring products, but the major two isomers proved to be inseparable and could not be identified conclusively. Phenylacetylene and trimethylsilylacetylene both appear to give modest yields of seven-membered ring products; however, the product mixture could not be conclusively identified. Highly electron deficient alkynes such as DMAD still fail to yield tractable material.

The synthesis of other unsymmetrical cobaltocenes was also successful, especially those starting from 1,1'-bis(*t*-butyl)cobalticenium **358**. Addition of methyllithium to this complex in THF at low temperature (-78°C) yields a 8:1 mixture of isomeric products **359A** and **359B**, obtained as a red oil in 93% yield (Eq. **136**). The major isomer is identified as (1-*t*-butyl-$C_5H_4$)Co(2-*t*-butyl-5-*exo*-methyl-1,3-cyclopentadiene) (**359A**) by $^1H$ NMR spectroscopy, while the minor complex is tentatively identified as the 1,2-isomer **359B**.



**358** **359A** **359B**

(Eq. 136)

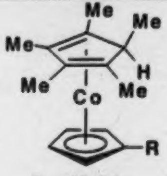
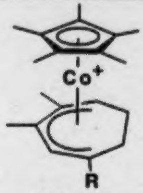
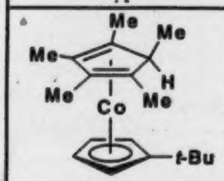
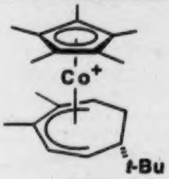
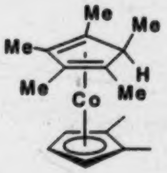
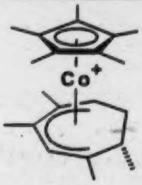
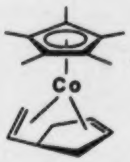
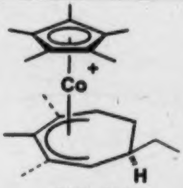
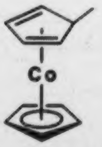
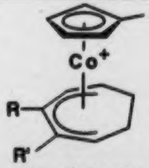
However, treatment of this mixture with $HBF_4{\bullet}Et_2O$ in the presence of various alkynes returns only inseparable mixtures of isomeric seven-membered ring products. The full assignment of the signals in the $^1H$ NMR spectrum proved prohibitively difficult, so these complexes remain uncharacterized. The most likely assessment is that the two major observed products are substitutional isomers of a *t*-butylcycloheptadienyl ligand.

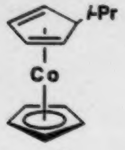
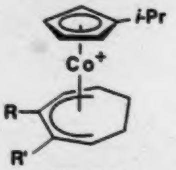
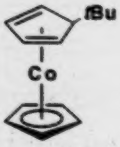
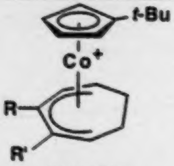
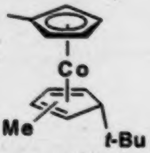
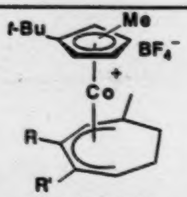
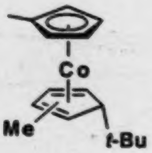
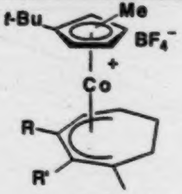
However, the possibility of products arising from ring opening of both monosubstituted and disubstituted cyclopentadiene ligands cannot be excluded. Minor components in the mixture are attributed to the reaction of the minor isomer with $HBF_4 \bullet BF_4$ and alkyne. In spite of the difficulties with certain templates, a large number of examples of this [5 + 2] cyclopentadiene/alkyne cycloaddition ring-expansion reaction have been demonstrated, as summarized in Table **14**.

Other five-membered ring diene substrates were also briefly investigated. The synthesis of $(C_5Me_5)Co(\eta^5\text{-indenyl})^+PF_6^-$ is readily accomplished from $[(C_5Me_5)CoCl]_2$ and indenyllithium, followed by oxidation with $NH_4PF_6$.[239] This cation may form an $\eta^3$-cyclopentenyl intermediate thermally if ring slippage of the indenyl ligand is a significant process. Thus, thermolysis of the complex in the presence of an alkyne may result in a ring expansion. No reaction of this complex with alkyne was noted at room temperature, but unfortunately the $PF_6^-$ counterion appears to decompose under thermolysis conditions ($C_6H_5Cl$, 100-110°C, excess alkyne). The $^1H$ NMR spectrum of the product was almost identical to the starting material, but the solubility properties had changed significantly. The tetraphenylborate salt was thus synthesized, but this complex also undergoes substantial decomposition to unidentified materials upon thermolysis in the presence of alkyne. Related complexes, such as the bis(indenyl)cobalt(III) salts[238] also decompose under these reaction conditions.

Other cycloalkadiene templates were subject to conditions favoring production of cycloheptadienyl complexes. However, the reaction of $(\eta^5\text{-}C_5Me_5)Co(\eta^4\text{-cyclohexadiene})$[240] with $HBF_4 \bullet Et_2O$ in the presence of 2-butyne does not yield tractable products. A single product is obtained from the reaction of $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-cyclohexadiene})$ **360**,[95a,117g] $HBF_4 \bullet Et_2O$ and 2-butyne in $CH_2Cl_2$, although the product **361** is not the result of ring expansion (Eq. **137**). The allyl olefin structure of **361** is suggested by the appearance of a lone quartet ($\delta$ 5.23, $J = 6.5$ Hz, 1H) and a corresponding methyl doublet ($\delta$ 2.06, $J = 6.3$ Hz) in the $^1H$ NMR spectrum. Several

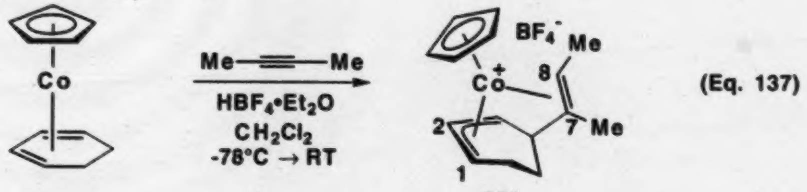
**Table 14.** $\eta^5$-Cycloheptadienyl Complexes Obtained from [5 + 2] Cyclopentadiene/ Alkyne Cycloaddition Reactions

| starting diene | product |
|---|---|
|  Me<br>Me<br>Me<br>Me<br>H<br>Me<br>Co<br>R<br>R = H, Me<br>A |  <br>193, 303 |
|  Me<br>Me<br>Me<br>Me<br>H<br>Me<br>Co<br>t-Bu<br>A |  <br>304 |
|  Me<br>Me<br>Me<br>Me<br>H<br>Me<br>Co<br>A |  <br>87 |
|  <br>A |  <br>309, 310 |
|  <br>B |  <br>320, 322-325 |

| starting diene | product |
|---|---|
|  <br>C |  <br>327-330 |
|  <br>A, B |  <br>331-337 |
|  <br>A, D |  t-Bu<br>Me<br>BF₄⁻<br>+<br>Co<br>R<br>R'<br>349, 351-354 |
|  <br>E |  t-Bu<br>Me<br>BF₄⁻<br>+<br>Co<br>R<br>R'<br>350, 355-357 |
|  |  |

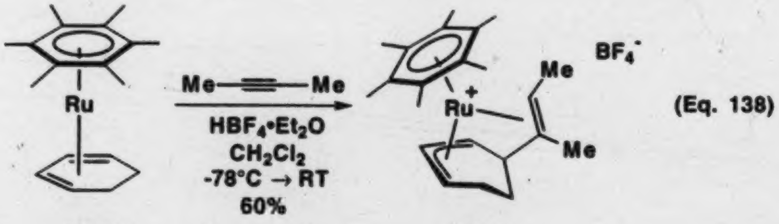
Alkynes used: (A) MeC≡CMe. (B) *t*-BuC≡CH, *t*-BuC≡CMe, PhC≡CPh, TMSC≡CMe, TMSC≡CTMS. (C) *t*-BuC≡CH, *t*-BuC≡CMe, TMSC≡CMe. (D) *t*-BuC≡CMe, PhC≡CPh, PhC≡CMe, cyclooctyne. (E) *t*-BuC≡CMe, *t*-BuC≡CH, TMSC≡CMe, MeC≡C(CO2Et). Conditions: $CH_2Cl_2$, -78°C→RT, 2 equiv $HBF_4\bullet Et_2O$, 3-7 equiv alkyne, 16 h.

resonances at δ 6.34 ($H_2$), 5.66 ($H_3$), and 5.15 ($H_1$) have chemical shifts and multiplicities consistent with the allyl protons. However, the remainder of the spectrum consists mainly of broad signals or multiplets. The $^{13}C$ NMR spectrum contains four doublets at δ 88.5 ($C_8$), 85.0 ($C_1$), 82.7 ($C_3$) and 80.3 ($C_2$), all of which are $sp^2$ hybridized carbon atoms according to the respective $^1J_{CH}$ values of 165, 169, 164 and 161 Hz.



**360** **361**

While the assigned structure of the cobalt complex **361** was still somewhat uncertain, ($\eta^6$-hexamethylbenzene)ruthenium($\eta^4$-cyclohexadiene) **362**[241] was subjected to the same reaction conditions to help confirm the structure of the cobalt complex (Eq. **138**). The ruthenium $\eta^3$-cyclohexenyl structure **363** was more easily determined, in large part because more of the signals in the $^1H$ NMR spectrum are well-resolved. The respective $^1H$ NMR and $^{13}C$ NMR spectral data for **361** and **363** are very similar, lending support to the assignment of the cobalt product **361**. Although the reactions of the cobalt complex **360** with $HBF_4•Et_2O$ in the presence of other alkynes does not produce tractable products, other work in this group has shown that the reactivity of the ruthenium system is more general. Thus, the reaction of ruthenium complex **362** with tetrafluoroboric acid and excess acetylene gives the analogous $\eta^2$,$\eta^3$-vinylcyclohexenyl complex.[120]



**362** **363**

The reaction of larger ring cobalt diene complexes with $HBF_4$•$Et_2O$ and 2-butyne in $CH_2Cl_2$ for the most part fails to give tractable products. (Cyclopentadienyl)cobalt($\eta^4$-cycloheptadiene), prepared by ligand exchange of cycloheptadiene with $(C_5H_5)Co(\eta^2$-$C_2H_4)_2$, for example, reacts with tetrafluoroboric acid in dichloromethane in the presence of excess 2-butyne, but does not yield tractable material. The reaction of $(\eta^5$-$C_5H_5)Co(\eta^4$-1,5-cyclooctadiene), prepared by similar methodology, with $HBF_4$•$Et_2O$ and 2-butyne under identical conditions appears to provide a very small amount of a product that is tentatively assigned as an $\eta^2$-vinyl-$\eta^3$-allyl complex analogous to **310** based on the analysis of the $^1H$ NMR spectrum. However, only a small amount of this material is formed and it could not be separated from impurities. Further investigation was not pursued.

### *III. Future Work*

Because the *t*-butyl-methylcyclopentadienyl system shows the greatest tolerance towards functional groups on the alkyne, the further development of this and closely related ligand systems may prove valuable. A critical requirement for this process is to develop conditions that produce a single isomer of the cyclopentadiene starting complex. A particularly interesting ligand is 1,3-bis(trimethylsilyl)cyclopentadiene. This ligand may be large enough to isolate a cobalt(II) dimer analogous to $[Cp^*CoCl]_2$. This would greatly simplfy the synthesis of mixed cyclopentadienyl systems. However, the main benefit is that the trimethylsilyl groups may be hydrolytically removed once the seven-membered ring is formed, reducing the number of potential isomers. It is also worthwhile to assay complexes of other electrophilic metal complexes (*e.g.*, iron) to ascertain the generality of this process.

As well, several important substrate classes may also undergo ring opening reactions, such as tetrahydroindene complexes. The use of diene complexes such as furan, pyrrole, or other aromatic heterocycles in this reactivity pattern could also possibly produce seven-membered heterocyclic complexes.

Using alkynes that are tethered to the cyclopentadiene ring may allow the development of an intramolecular version of this reaction and, not incidently, form synthetically valuable bicyclic product complexes. A more probable route for the introduction of heteroatoms is the incorporation of a heteroatom into the tether chain.

In examining the [3 + 2 + 2] cycloaddition chemistry of ($\eta^5$-$C_5Me_5$)cobalt(III) allyl templates with alkynes, we have demonstrated the facile preparation of an impressively large number of ($C_5Me_5$)Co($\eta^5$-cycloheptadienyl) complexes. It was shown that this chemistry can be expanded into the more readily available (cyclopentadienyl)cobalt(III) allyl template. These seven-membered ring complexes can be further functionalized by the reaction with carbon nucleophiles, generating a cycloheptadiene ligand. Finally, the intact organic ligand can be removed from the metal template without isomerization of the diene moiety, providing a new and relatively straightforward synthesis of seven-membered carbocycles.

Further study of several anomalous products obtained from these [3 + 2 + 2] allyl/alkyne cycloaddition reactions led to the development of a conceptually new [5 + 2] cycloaddition reaction between a cyclopentenylcobalt template and an alkyne. In this process, a coordinated cyclopentadiene ligand is protonated by strong acid, which yields a highly reactive cyclopentenylcobalt intermediate. Coordination and insertion of an alkyne into this intermediate ultimately form an $\eta^5$-cycloheptadienyl complex via a selective activation of an unstrained carbon-carbon bond. Various templates, such as 1-alkylcyclopentadiene complexes **314**, **315**, and **316**, were assayed in this reactivity pattern and a surprising degree of generality was found. However, the reaction of more highly substituted cyclopentadiene complexes such as **348** with alkynes is found to give regioisomeric mixtures of seven-membered ring products.

## Experimental Procedures

**Reagents and Methods.** All manipulations on air sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques, or in a Vacuum Atmospheres He-553-2 Dri-lab equipped with a Mo-41-1 inert gas purifier and a CD-882 Dri-Cold Freezer maintained at -35 °C. Vacuum transfer of volatile reagents was performed at high vacuum ($10^{-5}$ mm Hg) using a MKS Baratron digital pressure transducer for measurement of gas pressure in known volume flasks. Toluene, benzene, tetrahydrofuran, diethyl ether, hexane and pentane were distilled from sodium/ benzophenone ketyl or sodium (potassium)/benzophenone ketyl. Reagent grade acetone was degassed and stored under nitrogen with no further purification. Dichloromethane and acetonitrile were distilled from calcium hydride and degassed. Unless stated otherwise, all reactions were carried out under a nitrogen atmosphere. Photolysis was carried out using a Hanovia 450 watt high pressure mercury lamp filtered through pyrex. IR spectra were recorded on a Nicolet Magna IR 750 or a Nicolet 20SX spectrophotometer. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AM-400 ($^1$H, 400 MHz; $^{13}$C, 100 MHz), Bruker AM-360 ($^1$H, 360 MHz), Bruker AM-300 ($^1$H, 300 MHz; $^{13}$C, 75 MHz), Bruker AM-200 ($^1$H, 200 MHz; $^{13}$C, 50 MHz), Varian Unity-500 ($^1$H, 500 MHz; $^{13}$C, 125 MHz), or a Varian Unity-Inova 300 ($^1$H, 300 MHz) spectrometer. Chemical shifts are reported in ppm relative to external TMS using residual protiated solvent resonances as internal reference. Mass spectra were obtained on a Kratos MS-50 spectrometer or by positive mode electrospary ionization on a Micromass ZabSpec Hybrid Sector-TOF. FAB mass spectra were recorded on an AEIMS9 spectrometer. Elemental analyses were performed by the University of Alberta Microanalysis Laboratories.

**Further Note on Spectroscopic Methods.** In $^1H$ NMR spectral data, values of the coupling constants are either obtained directly from the spectrum, or extracted using standard homonuclear decoupling techniques. Although generally measured to ± 0.1 Hz, $J$ values are self-consistent only to ± 1Hz. GCOSY denotes the standard COSY experiment, aquired using field gradients. Data for the $^1H$-$^1H$ COSY or GCOSY is presented such that correlations are listed only once. Values of $^1J_{CH}$ are obtained either directly from the gated decoupled spectrum, or from the coupled HMQC spectrum. $^1H$-$^{13}C$ HETCORR experiments are recorded at the $^{13}C$ frequency of the spectrometer, while HMQC and HMBC are recorded at the $^1H$ frequency.

**Atom labels for numbering system of cycloheptadienyl complexes.** To aid in tabulation of $^1H$ NMR spectral information, a common numbering scheme was devised based on the conformation of the seven-membered ring. The most upfield signal in the $^1H$ NMR spectrum was assigned to the $H_{6exo}$ atom. This was determined based on careful correlation of the $J_{H-H}$ values to the Karplus value obtained from the torsional angle between the relevant H atoms obtained from X-ray crystallographic structures. In cases where the cycloheptadienyl ligand has a mirror plane, this artifice is maintained and the signals are assigned to the two related positions.

The following compounds were prepared by published procedures: $(C_5Me_5)Co(C_2H_4)_2$(**79**),[90] $(C_5Me_5)Co(\eta^3\text{-}C_3H_5)(OTf)$ (**80**),[62,89] $(C_5Me_5)Co(\eta^3\text{-1-Me-}C_3H_4)(OTf)$ (**81**),[88,89] $(C_5Me_5)Co(\eta^3\text{-1,2-}Me_2C_3H_3)(OTf)$ (**85**),[88,89] $(C_5Me_5)Co(\eta^3\text{-1,3-}Me_2C_3H_3)(OTf)$ (**86**),[88] $(C_5Me_5)Co(\eta^4$-cycloheptatriene) (**100**),[109] 1-(bromomethyl)-1-cyclopentene (**109**),[112,113] 1-(hydroxymethyl)-3,4-dihydronaphthalene (**115**),[114] $(C_5H_5)Co(C_2H_4)_2$ (**123**),[117] $(C_5H_5)Co(\eta^3\text{-}C_3H_5)(Br)$ (**125**),[117] bicyclo[3.2.0]heptadiene (**295**),[223] $(C_5H_5)Co(\eta^4$-cyclohexadiene) (**309**),[95a,117g] $(C_6Me_6)Ru(\eta^4$-cyclohexadiene) (**311**),[240] cyclooctyne,[97] $[(C_5Me_5)CoCl]_2$,[106] $(C_5H_5)Co(\eta^4$-cycloheptatriene),[118]

$(C_5Me_5)Co(\eta^4$-4-vinyl-1-cyclopentene),[128] hexadeuteriocyclopentadiene,[229] 1,2-dimethylcyclopentadiene,[230] $(C_5Me_5)Co(\eta^4$-cyclohexadiene),[240] $[(C_6Me_6)RuCl_2]$,[241] $C_5Me_5H$,[242] $(C_5H_5)_2Fe^+ PF_6^-$,[243] $[(C_5Me_5)IrCl_2]_2$.[244]

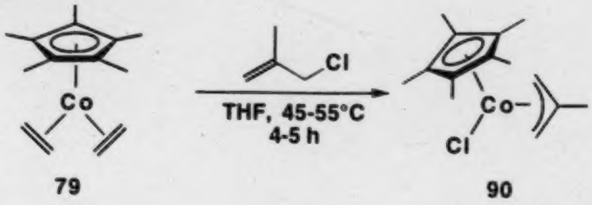
$(C_5Me_5)Co(\eta^4$-butadiene) (**82**),[88,89] $(C_5Me_5)Co(\eta^4$-isoprene) (**83**),[88,89] and $(C_5Me_5)Co(\eta^4$-1,3-pentadiene) (**84**),[88,89] were prepared by thermal exchange of the ethylene ligands in $(C_5Me_5)Co(C_2H_4)_2$ (**79**) with the appropriate diene in hexanes at 60-70°C. Complexes **82**[106] and **83**[84] have been previously prepared by different methodology. 1-(Bromomethyl)-1-cyclohexene (**103**) was prepared by NBS bromination of methylenecyclohexane.[110,111] 1-Vinyl-1-cyclopentene[116] was prepared by $H_2SO_4$ catalyzed dehydration of 1-vinyl-1-cyclopentanol, which itself was the product of the reaction of vinylmagnesium bromide with cyclopentanone. Sodium dimethylmalonate was prepared in the drybox by the addition of NaH to a THF solution of the organic ester. The lithium enolate of acetophenone was prepared in the drybox by the addition of LDA to a pentane solution of the ketone. Trityl tetrafluoroborate was prepared by the addition of $HBF_4$ to a solution of triphenylmethanol in acetic anhydride, followed by washing the precipitate with copious amounts of diethyl ether.

Cobaltocene was made by the addition of solid anhydrous $CoCl_2$ to a solution of NaCp in THF/DME.[245] Cobalticenium chloride was prepared by oxidation of this solution with aqueous HCl and air.[245] The cobalticenium $PF_6^-$ salt was precipitated from aqueous solution with $NH_4PF_6$. 1,1'-Dimethylcobalticenium was prepared analogously using sodium methylcyclopentadienide.[245] Methylcyclopentadienylcobalt complexes were prepared following the published procedured for the $C_5H_5$ analogues.[117]

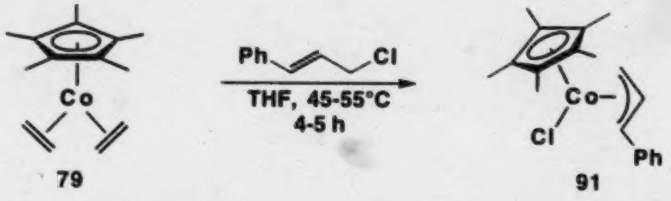
*t*-Butylcyclopentadiene was prepared by quenching *t*-BuCpLi[246] with water. (Trimethylsilyl)-cyclopentadiene was prepared by the addition of TMSCl to NaCp. Carbomethoxycyclopentadiene was prepared by the addition of diethylcarbonate to NaCp.[247] All cyclopentadienes were distilled before use.

$(C_5H_5)Co(\eta^4$-alkylcyclopentadiene) (R = H, Me, *i*-Pr, *t*-Bu) compounds were prepared from addition of alkyllithium or alkylmagnesium halide reagents to a slurry of $(C_5H_5)_2Co^+$ in THF at -78 °C. Workup consisted of removing the THF solvent, and extraction of the residue with pentane. The pentane extracts were filtered through a Celite pad and dried. These compounds have been previously prepared using a similar procedure.[93g]

## Chapter 2 Experimental Section

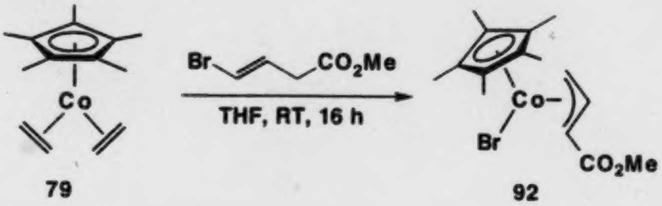


**$(C_5Me_5)Co(2\text{-}Me\text{-}C_3H_4)Cl$ (90).** In a Schlenk flask, $(C_5Me_5)Co(C_2H_4)_2$ **(79)** (0.2998 mg, 1.198 mmol) was dissolved in tetrahydrofuran (15 mL) under a nitrogen atmosphere. 1-Chloro-2-methyl-2-propene (180 µl, 1.83 mmol, 1.5 equiv) was added by syringe and the solution was then heated to 45-55 °C with stirring for 4-5 h. All volatile material was removed *in vacuo* and the the residue was extracted with toluene. The combined extracts were filtered through a Celite pad. Removal of the solvent gave a dark red-black solid (241 mg, 71%). $^1H$ NMR (400 MHz, $C_6D_6$) δ 3.69 (s, 2H, $H_a$), 3.12 (s, 2H, $H_s$), 1.43 (s, 3H, $CH_3$), 1.24 (s, 15H, $C_5\underline{Me_5}$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 111.2 ($C_c$), 93.9 ($\underline{C_5}Me_5$), 56.8 ($C_t$), 24.2 ($\underline{C}H_3$), 10.2 ($C_5\underline{Me_5}$). Analysis calculated for $C_{14}H_{22}ClCo$: C, 59.06; H, 7.79; found: C, 59.015; H, 7.886.

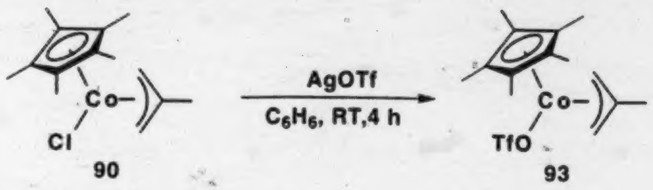


**$(C_5Me_5)Co(1\text{-}Ph\text{-}C_3H_4)Cl$ (91).** In a Schlenk flask, $(C_5Me_5)Co(C_2H_4)_2$ **(79)** (0.3458 g, 1.382 mmol) was dissolved in tetrahydrofuran (20 mL) under a nitrogen atmosphere. Cinnamyl chloride (210 µl, 1.51 mmol, 1.09 equiv) was added via syringe. The solution was then heated to 45-55 °C with stirring for 4-5 h. All volatile material was removed *in vacuo*. The residue was extracted with toluene and the toluene solution was filtered through a Celite pad. Removal of the solvent gave a dark purple-black solid (334.0 mg, 70%). $^1H$ NMR (400 MHz, $C_6D_6$) δ 7.51 (d, $J = 7.1$ Hz, 2H, $H_{Ph}$), 7.13-7.21 (m, 3H,

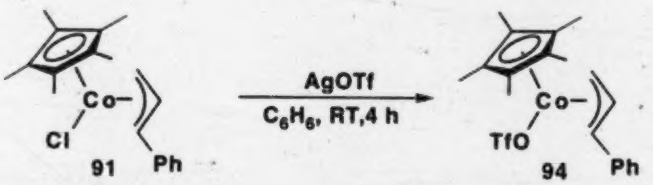
$H_{Ph}$), 4.66 (d, $J$ = 12.9 Hz, 1H, $H_1$), 4.52 (td, $J$ = 12.2, 7.5 Hz, 1H, $H_2$), 3.97 (d, $J$ = 7.6 Hz, 1H, $H_{3a}$), 3.32 (d, $J$ = 12.2 Hz, 1H, $H_{3s}$), 1.05 (s, 15H, $C_5\underline{Me_5}$); $^{13}C$ NMR (100 MHz, $C_6D_6$) δ 141.3 ($C_{ipso}$), 129.1 ($C_{Ph}$), 127.0 (overlap with solvent peak, $C_{Ph}$), 126.3 ($C_{Ph}$), δ 93.2 ($\underline{C_5}Me_5$), 91.2 ($C_2$), 78.2 ($C_1$), 56.8 ($C_3$), 8.8 ($C_5\underline{Me_5}$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 140.5 ($C_{ipso}$), 129.1 ($C_{Ph}$), 126.9 ($C_{Ph}$), 126.6 ($C_{Ph}$), 93.6 ($\underline{C_5}Me_5$), 91.5 ($C_2$), 78.5 ($C_1$), 57.0 ($C_3$), 9.0 ($C_5\underline{Me_5}$). Analysis calculated for $C_{19}H_{24}ClCo$: C, 65.81; H, 6.98; found: C, 65.409; H, 6.500.



**($C_5Me_5$)Co(1-($CO_2Me$)-$\eta^3$-$C_3H_4$)(Br) (92).** To a solution of ($C_5Me_5$)Co($C_2H_4$)$_2$ **(79)** (0.2356 g, 0.9414 mmol) in tetrahydrofuran (10 mL) under a nitrogen atmosphere was added methyl 4-bromocrotonate (0.11 mL, 1.0 equiv). The orange solution slowly changed color to dark purple as the reaction was allowed to stir at room temperature overnight. All volatile material was removed *in vacuo* and the residue was crystallized from diethyl ether/pentane. Dark purple crystals (0.2868 g, 82%) were obtained. IR ($CH_2Cl_2$ cast, $cm^{-1}$) 2952 (w), 2916 (w), 1699 (s), 1506 (m), 1442 (m), 1378 (m), 1314 (s), 1251 (w), 1228 (m), 1187 (m), 1160 (s), 1074 (m), 1043 (m), 1021 (m), 985 (m), 959 (w), 901 (m), 839 (m), 721 (w), 558 (w); $^1H$ NMR (400 MHz, $CD_2Cl_2$) δ 5.01 (ddd, $J$ = 13.3, 11.6, 8.1 Hz, 1H, $H_c$), 4.00 (d, $J$ = 8.1 Hz, 1H, $H_s$), 3.80 (s, 3H, $CO_2\underline{Me}$), 3.16 (d, $J$ = 13.3 Hz, 1H, $H_a$), 2.98 (d, $J$ = 11.6 Hz, 1H, $H_a$), 1.58 (s, 15H, $C_5\underline{Me_5}$); $^{13}C$ NMR (100 MHz, $CD_2Cl_2$) δ 99.2, 95.2, 60.0, 57.4, 51.8, 9.7. The carbonyl carbon was not observed above baseline noise. MS m/z calculated for $C_{15}H_{22}CoO_2{}^{81}Br$ ($M^+$): 374.01147; found: 374.01107 (13%). MS m/z calculated for $C_{15}H_{22}CoO_2{}^{79}Br$ ($M^+$): 372.01352; found: 372.01275 (13%).

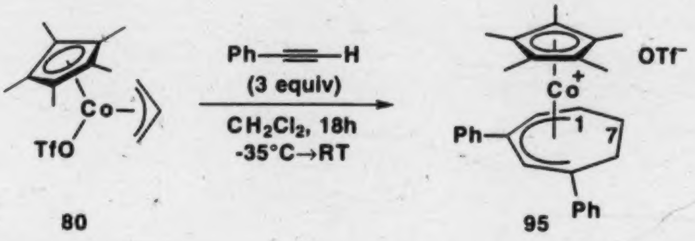


**$(C_5Me_5)Co(2\text{-}Me\text{-}\eta^3\text{-}C_3H_4)(OTf)$ (93).** In the drybox, $(C_5Me_5)Co(2\text{-}Me\text{-}\eta^3\text{-}C_3H_4)(Cl)$ (**90**) (59.1 mg, 0.208 mmol) was dissolved in benzene (10 mL). Silver triflate (62.1 mg, 2.41 mmol, 1.16 equiv) was added at room temperature. After stirring 4 h, the solution was filtered through a Celite pad. Removal of the solvent gave a dark brown powder (73.6 mg, 89%). The analytical sample was crystallized from toluene-pentane at -35 °C. $^1H$ NMR (360 MHz, $CD_2Cl_2$) δ 4.60 (s, 2H, $H_a$), 2.26 (s, 2H, $H_s$), 1.84 (s, 3H, $CH_3$), 1.46 (s, 15H, $C_5Me_5$); $^{13}C$ NMR (75 MHz, $C_6D_6$) δ 117.4 ($C_2$), 94.8 ($\underline{C_5}Me_5$), 60.6 ($C_1$), 23.5 (Me), 9.8 ($C_5\underline{Me_5}$). Triflate carbon was not located above baseline noise. Analysis calculated for $C_{15}H_{22}CoF_3O_3S$: C, 45.23; H, 5.57; found: C, 44.974; H, 5.866.



**$(C_5Me_5)Co(1\text{-}Ph\text{-}\eta^3\text{-}C_3H_4)(OTf)$ (94).** In the drybox, $C_5Me_5Co(1\text{-}Ph\text{-}\eta^3\text{-}C_3H_4)Cl$ (**91**) (43.0 mg, 0.124 mmol) was dissolved in benzene (10 mL). Silver triflate (37.5 mg, 0.146 mmol, 1.18 equiv) was added. After stirring 4 h, the solution was filtered through a Celite pad. Removal of the solvent gave a deep brown solid (43.3 mg, 76%). The analytical sample was recrystallized from toluene/pentane at -30°C. $^1H$ NMR (360 MHz, $C_6D_6$) δ 7.50 (d, $J$ = 7 Hz, 2H, $H_{Ph}$), 7.13-7.20 (m, 3H, $H_{Ph}$), 4.65 (d, $J$ = 12.8 Hz, 1H, $H_{1s}$), 4.52 (td, $J$ = 12.4, 7.5 Hz, 1H, $H_2$), 3.97 (d, $J$ = 7.5 Hz, 1H, $H_{3a}$), 3.32 (d, $J$ = 12.1 Hz, 1H, $H_{3s}$), 1.06 (s, 15H, $C_5\underline{Me_5}$); $^{13}C$ NMR (75 MHz, $C_6D_6$) δ 140.3 (s, $C_{Ph}$), 129.5 (dd, $^1J_{CH}$ = 157.0 Hz, $^2J_{CH}$ = 7.2 Hz, $C_{Ph}$), 128.3 (d, $^1J_{CH}$ = 157.1 Hz, $C_{Ph}$), 127.4 (dd,

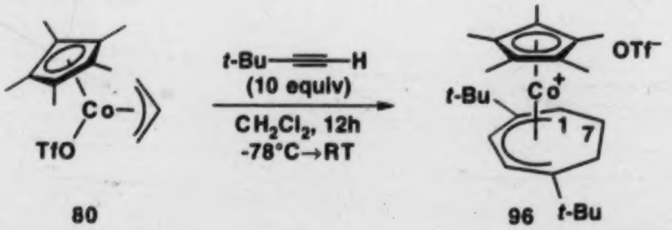
$^1J_{CH}$ = 156.9 Hz, $^2J_{CH}$ = 7.9 Hz, $C_{Ph}$), 95.3 (d, $^1J_{CH}$ = 157.1 Hz, $C_2$), 94.3 (s, $\underline{C}_5Me_5$), 80.9 (d, $^1J_{CH}$ = 158.9 Hz, $C_1$), 60.6 (t, $^1J_{CH}$ = 161.6 Hz, $C_3$), 8.6 (q, $^1J_{CH}$ = 127.6 Hz, $C_5\underline{Me}_5$). Analysis calculated for $C_{20}H_{24}CoF_3O_3S$: C, 52.18; H, 5.25; found: C, 51.854; H, 5.019.



**[(C$_5$Me$_5$)Co($\eta^5$-3,5-Ph$_2$C$_7$H$_7$ )]$^+$ OTf$^-$ (95).** *Method A.* $(C_5Me_5)Co(C_3H_5)(OTf)$ **(80)** (94.6 mg, 0.246 mmol) was dissolved in dichloromethane (10 mL) under a nitrogen atmosphere and cooled to -78 °C. Phenylacetylene (10 equiv) was added via syringe and the solution was warmed slowly to room temperature. All volatile material was removed *in vacuo* and the residue was purified by repeated column chromatography, using 4% methanol/ dichloromethane on silica gel. The isolated yield of dark red-black material was 52.0 mg (36%).

**[(C$_5$Me$_5$)Co($\eta^5$-3,5-Ph$_2$C$_7$H$_7$ )]$^+$ OTf$^-$ (95).** *Method B.* $(C_5Me_5)Co(C_3H_5)(OTf)$ **(80)** (38.9 mg, 0.101 mmol) was dissolved in dichloromethane (5 mL) and cooled to -78 °C in a dry-ice/acetone bath. To this solution was added phenylacetylene (33 µL, 0.303 mmol, 3 equiv) and the solution was kept at -78 °C for 10 min. The flask was transferred to an acetone bath held at -30 °C and stirred overnight at that temperature. The solution was then allowed to warm to room temperature and stirred 4 h. The solvent was removed and the product purified as detailed above. The isolated yield was 34.6 mg (58%). IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3061 (w), 2963 (w), 2919 (w), 1487 (m), 1454 (m), 1429 (m), 1381 (m), 1262 (s), 1075 (w), 1055 (w), 1030 (s), 1002 (w), 768 (m), 734 (m), 698 (m), 656

(w), 637 (s), 572 (w), 547 (w), 516 (m); $^1$H NMR (300 MHz, $CD_2Cl_2$) δ 8.1-7.4 (m, 10H, $H_{aromatic}$), 6.47 (br s, 1H, $H_4$), 5.10 (d, $J_{2\text{-}1}$ = 9.5 Hz, 1H, $H_2$), 4.74 (m, dddd by decoupling, $J_{1\text{-}2}$ = 9.4 Hz, $J_{1\text{-}7exo}$ = $J_{1\text{-}7endo}$ = 3 Hz, $J_{1\text{-}6endo}$ = 2 Hz), 3.24 (dddd, $J_{7endo\text{-}7exo}$ = 16.9 Hz, $J_{7endo\text{-}6exo}$ = 12.2 Hz, $J_{7endo\text{-}6endo}$ = 7.0 Hz, $J_{7endo\text{-}1}$ = 2.4 Hz, 1H, $H_{7endo}$), 2.69 (dddd, $J_{7exo\text{-}7endo}$ = 17.0 Hz, $J_{7exo\text{-}6exo}$ = $J_{7exo\text{-}6endo}$ = 4.1 Hz, $J_{7exo\text{-}4}$ < 1Hz, 1H, $H_{7exo}$), 2.04 (ddd, $J_{6endo\text{-}6exo}$ = 13 Hz, $J_{6endo\text{-}7endo}$ = 6.9 Hz, $J_{6endo\text{-}1}$ = 1.6 Hz, 1H, $H_{6endo}$), 1.26 (s, 15H, $C_5Me_5$), 0.58 (ddd, $J_{6exo\text{-}7exo}$ = 4.5 Hz, $J_{6exo\text{-}6endo}$ = $J_{6exo\text{-}7endo}$ = 13.1 Hz, 1H, $H_{6exo}$); $^1$H-$^1$H COSY (400 MHz, $CD_2Cl_2$) δ 6.47 ($H_4$) ↔ δ 5.10 (w, $H_2$), δ 2.0 (w, $H_{6endo}$), δ 0.58 (w, $H_{6exo}$); δ 5.10 ($H_2$) ↔ δ 2.69 (w, $H_{7exo}$); δ 4.74 ($H_1$) ↔ δ 3.24 ($H_{7endo}$), δ 2.69 ($H_{7exo}$), δ 2.04 ($H_{6endo}$); δ 3.24 ($H_{7endo}$) ↔ δ 2.69 ($H_{7exo}$), δ 2.04 ($H_{6endo}$), δ 0.58 ($H_{6exo}$); δ 2.69 ($H_{7exo}$) ↔ δ 0.58 ($H_{6exo}$); δ 2.04 ($H_{6endo}$) ↔ δ 0.58 ($H_{6exo}$); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) δ 140.1 (s, $C_{Ph,\ ipso}$), 134.0 (s, $C_{Ph,\ ipso}$), 131.6 (d, $^1J_{CH}$ = 166 Hz, $C_{Ph,\ para}$), 130.4 (d, $^1J_{CH}$ = 160.7 Hz, $C_{Ph,\ para}$), 129.9 (d, $^1J_{CH}$ = 166 Hz, $C_{Ph,\ meta}$), 129.8 (d, $^1J_{CH}$ = 166 Hz, $C_{Ph,\ meta}$), 128.1 (d, $^1J_{CH}$ = 156.5 Hz, $C_{Ph,\ ortho}$), 125.4 (d, $^1J_{CH}$ = 157.4 Hz, $C_{Ph,\ ortho}$), 114.5 (s, $C_3$), 107.9 (s, $C_5$), 98.1 (s, $\underline{C_5}Me_5$), 91.8 (d, $^1J_{CH}$ = 163.3 Hz, $C_4$), 87.9 (d, $^1J_{CH}$ = 145.5 Hz, $C_1$), 86.0 (d, $^1J_{CH}$ = 156.3 Hz, $C_2$), 46.2 (t, $^1J_{CH}$ = 132.2 Hz, $C_7$), 32.2 (t, $^1J_{CH}$ = 133.2 Hz, $C_6$), 8.6 (q, $^1J_{CH}$ = 128.9 Hz, $C_5\underline{Me_5}$). EMFAB MS calculated for $C_{29}H_{32}Co$ ($M^+$ - $^-$OTf): 439.1836; found: 439.1828. Analysis calculated for $C_{30}H_{32}CoF_3O_3S$: C, 61.22; H, 5.48; Found: C, 61.064; H, 5.587.



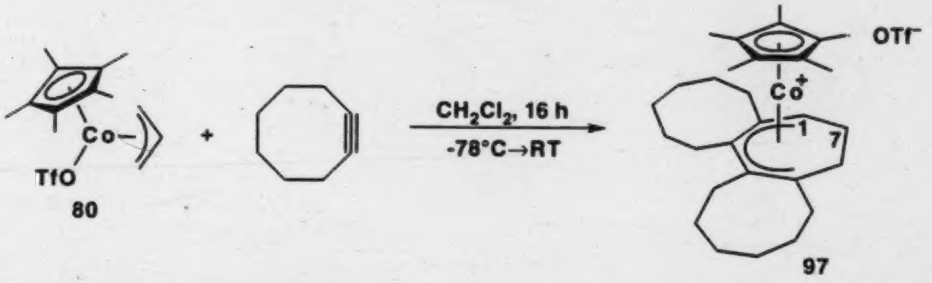
80

96

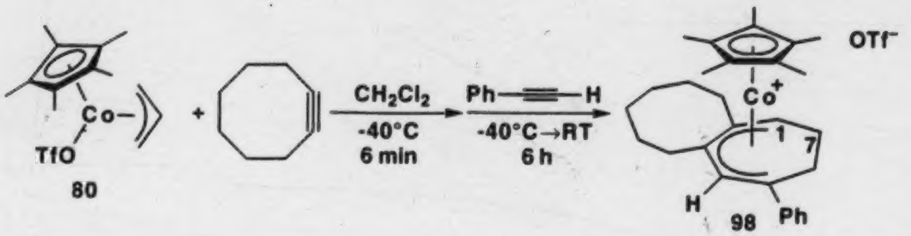
**$[(C_5Me_5)Co(2,5\text{-}^tBu_2\text{-}\eta^5\text{-}C_7H_7)]^+$ $TfO^-$.(96).** This complex has previously been prepared and spectroscopically characterized.[88] In the drybox, $(C_5Me_5)Co(\eta^3$-

$C_3H_5$)(OTf) (303 mg, 0.788 mmol) was placed in a Kontes flask. The flask was removed to the Schlenk line and dichloromethane (8 mL) was added. On the high vacuum line, 3,3-dimethyl-1-butyne (0.650 g, 7.95 mmol) was added by vacuum transfer. The solution was warmed to -78 °C, and then allowed to warm slowly to room temperature while being stirred overnight. The solvent was evaporated, the residue washed with diethyl ether and then dissolved in dichloromethane and filtered through Celite. Evaporation gave a green, air stable solid (379.1 mg, 88%). Another sample of the material, prepared in a similar manner, was purified by dissolving in a minimum amount of dichloromethane and adding dropwise to an excess of rapidly stirring diethyl ether to give a green powder in 30-40% yield. IR ($CH_2Cl_2$ cast, $cm^{-1}$) 2974 (m), 2908 (w), 2876 (w), 1467 (m), 1437 (w), 1376 (m), 1361 (w), 1267 (s), 1223 (m), 1147 (s), 1108 (w), 1031 (s), 1019 (m), 637 (s), 571 (w), 516 (m); $^1$H NMR (400 MHz, acetone-$d_6$) $\delta$ 7.41 (d, $J_{3\text{-}4}$ = 6 Hz, 1H, $H_3$), 5.40 ("dt" (ddd), $J_{4\text{-}3}$ = 6 Hz, $J_{4\text{-}6exo}$ = $J_{4\text{-}7endo}$ = 1.7 Hz, 1H, $H_4$), 4.79 (dd, $J_{1\text{-}7exo}$ = 6 Hz, $J_{1\text{-}7endo}$ = 1.4 Hz, 1H, $H_1$), 3.24 (dddd, $J_{7endo\text{-}7exo}$ = 17 Hz, $J_{7endo\text{-}6exo}$ = 12 Hz, $J_{7endo\text{-}1}$ = 1.4 Hz, $J_{7endo\text{-}4}$ = 1.7 Hz, 1H, $H_{7endo}$), 2.98 (dddd, $J_{7exo\text{-}7endo}$ = 17 Hz, $J_{7exo\text{-}1}$ = 6 Hz, $J_{7exo\text{-}6exo}$ = 2.6 Hz, $J_{7exo\text{-}6endo}$ = 3.6 Hz, 1H, $H_{7exo}$), 1.83 (s, 15H, $C_5\underline{Me_5}$), 1.8 (m, 1H, $H_{6endo}$, partially obscured), 1.33 (s, 9H, $Me_9$), 1.16 (s, 9H, $Me_{11}$), -0.19 (br "dt", $J_{6exo\text{-}7endo}$ = $J_{6exo\text{-}6endo}$ = 12, $J_{6exo\text{-}7exo}$ = 3 Hz, 1H, $H_{6exo}$); $^1$H-$^1$H COSY (400 MHz, acetone-$d_6$) $\delta$ 7.41 ($H_3$) ↔ $\delta$ 5.40 ($H_4$), $\delta$ 4.78 (w, $H_1$), $\delta$ -0.19 (w, $H_{6exo}$); $\delta$ 5.40 ($H_4$) ↔ $\delta$ 3.24 (w, $H_{7endo}$), $\delta$ -0.19 (w, $H_{6exo}$); $\delta$ 4.78 ($H_1$) ↔ $\delta$ 3.24 ($H_{7endo}$), $\delta$ 2.98 ($H_{7exo}$); $\delta$ 3.24 ($H_{7endo}$) ↔ $\delta$ 2.98 ($H_{7exo}$), $\delta$ -0.19 ($H_{6exo}$); $\delta$ 2.98 ($H_{7exo}$) ↔ $\delta$ -0.19 ($H_{6exo}$); $^{13}$C NMR (100 MHz, acetone-$d_6$) $\delta$ 186.3 (s, $C_5$), 125.2 (s, $C_2$), 96.3 (s, $\underline{C_5}Me_5$), 85.7 (d, $J_{C\text{-}H}$ = 161 Hz, $C_4$), 85.0 (d, $J_{C\text{-}H}$ = 168 Hz, $C_3$), 69.3 (d, $J_{C\text{-}H}$ = 149 Hz, $C_1$), 57.3 (t, $J_{C\text{-}H}$ = 129 Hz, $C_7$), 42.7 (s, $C_{10}$), 37.7 (s, $C_8$), 31.2 (q, $J_{C\text{-}H}$ = 125 Hz, $C_9$), 28.3 (t, $C_6$), 27.4 (q, $J_{C\text{-}H}$ = 130 Hz, $C_{11}$), 10.9 (q, $J_{C\text{-}H}$ = 128 Hz, $C_5\underline{Me_5}$); $^1$H-$^{13}$C HETCORR (100 MHz, acetone-$d_6$) $\delta$ 85.7 ($C_4$) ↔ $\delta$ 5.40 ($H_4$); $\delta$ 85.0 ($C_3$) ↔ $\delta$ 7.41 ($H_3$); $\delta$ 69.3 ($C_1$) ↔ $\delta$ 4.79 ($H_1$); $\delta$ 57.3 ($C_7$) ↔ $\delta$ 3.24 ($H_{7endo}$), $\delta$ 2.98 ($H_{7exo}$); $\delta$ 31.2 ($C_9$) ↔ $\delta$ 1.33 ($Me_9$);

δ 28.3 ($C_6$) ↔ δ 1.8 ($H_{6endo}$), δ -0.19 ($H_{6exo}$); δ 27.4 ($C_{11}$) ↔ δ 1.16 ($Me_{11}$), δ -0.19 ($H_{6exo}$); δ 10.9 ($C_5\underline{Me_5}$) ↔ δ 1.83 ($C_5\underline{Me_5}$); $^1H$-$^{13}C$ Long Range HETCORR (100 MHz, acetone-$d_6$) δ 186.3 ($C_5$) ↔ δ 7.41 ($H_3$), δ 1.16 ($Me_{11}$); δ 125.2 ($C_2$) ↔ δ 5.40 ($H_4$), δ 1.33 ($Me_9$); δ 96.3 ($\underline{C_5}Me_5$) ↔ δ 1.83 ($C_5\underline{Me_5}$); δ 85.7 ($C_4$) ↔ δ 1.8 ($H_{6endo}$), δ -0.19 ($H_{6exo}$); δ 85.0 ($C_3$) ↔ δ 4.79 ($H_1$); δ 69.3 ($C_1$) ↔ δ 7.41 ($H_3$), δ 1.8 ($H_{6endo}$); δ 57.3 ($C_7$) ↔ δ -0.19 ($H_{6exo}$); δ 42.7 ($C_{10}$) ↔ δ 1.16 ($Me_{11}$); δ 37.7 ($C_8$) ↔ δ 1.33 ($Me_9$); δ 28.3 ($C_6$) ↔ δ 5.40 ($H_4$), δ 4.79 ($H_1$). Analysis calculated for $C_{26}H_{40}CoF_3O_3S$: C, 56.92; H, 7.35; S, 5.84 found: C, 56.753; H, 7.480; S, 5.702.

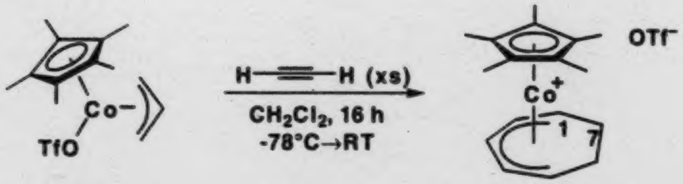


**[($C_5Me_5$)Co($\eta^5$-$C_{19}H_{29}$)]$^+$ OTf$^-$ (97).** In the drybox, ($C_5Me_5$)Co($\eta^3$-$C_3H_5$)(OTf) **(80)** (35.3 mg, 0.0918 mmol) was placed in a Schlenk flask capped with a rubber septum. The flask was removed to the Schlenk line where dichloromethane (2 mL) was added and the solution was cooled to -78 °C. Cyclooctyne (30 µL, *ca.* 0.3 mmol) was added and the reaction was allowed to warm slowly to room temperature overnight with stirring. The solvent was evaporated and the residue was washed with diethyl ether and then redissolved in dichloromethane and filtered through a Celite pad. Evaporation of the solvent gave an orange air stable foam (46.3 mg, 84%). IR ($CH_2Cl_2$ cast, cm$^{-1}$) 2993 (w), 2924 (s), 2857 (m), 1496 (m), 1481 (w), 1471 (w), 1456 (m), 1435 (m), 1379 (w), 1270 (s), 1220 (m), 1142 (s), 1114 (w), 1096 (m), 1072 (m), 1030 (s), 749 (w), 636 (s), 570 (w), 516 (w); $^1H$ NMR (400 MHz, acetone-$d_6$) δ 4.30 (br s, 1H, $H_1$), 3.20 (ddd, *J* = 14, 7, 2 Hz, 1H, ring $CH_2$), 3.0-2.8 (m, 4H), 2.95 (m, $H_{7endo}$), 2.55-2.45 (m, 1H, ring $CH_2$), 2.35 (dt, *J* = 16, 4 Hz, 1H, $H_{7exo}$), 2.25-2.15 (m, 1H, ring $CH_2$), 2.1-1.2 (sets of overlapping multiplets, ring $CH_2$'s), 1.75 (s, 15H, $C_5\underline{Me}_5$), 1.5 (m, obscured, $H_{6endo}$), 1.0-0.9 (m, 1H, ring $CH_2$), -0.06 (td, $J_{obs}$ = 12.2, 4.8, 1H, $H_{6exo}$); $^1H$-$^1H$ COSY (400 MHz, acetone-$d_6$, selected data only) $\delta$ 4.30 ($H_1$) $\leftrightarrow$ $\delta$ 2.95 ($H_{7endo}$), $\delta$ 2.35 ($H_{7exo}$), $\delta$ 1.50 ($H_{6endo}$), $\delta$ -0.06 ($H_{6exo}$); $\delta$ 3.20 ($CH_2$) $\leftrightarrow$ $\delta$ 2.97 ($CH_2$), $\delta$ 2.2 ($CH_2$), $\delta$ 1.6 ($CH_2$); $\delta$ 3.0 ($CH_2$) $\leftrightarrow$ $\delta$ 2.5 ($CH_2$), $\delta$ 1.7 ($CH_2$); $\delta$ 2.95 ($H_{7endo}$) $\leftrightarrow$ $\delta$ 2.35 ($H_{7exo}$), $\delta$ 1.50 ($H_{6endo}$), -0.06 ($H_{6exo}$); $\delta$ 2.9 $\leftrightarrow$ $\delta$ 1.95, $\delta$ 1.8, $\delta$ 1.55 (all $CH_2$); $\delta$ 2.35 ($H_{7exo}$) $\leftrightarrow$ $\delta$ 1.50 ($H_{6endo}$), $\delta$ -0.06 ($H_{6exo}$); $\delta$ 1.50 ($H_{6endo}$) $\leftrightarrow$ $\delta$ -0.06 ($H_{6exo}$); $^{13}C$ NMR (100 MHz, acetone-$d_6$) $\delta$ 119.1 (s, $C_3$), 111.2 (s, $C_{2/4/5}$), 107.3 (s, $C_{2/4/5}$), 105.7 (s, $C_{2/4/5}$), 97.8 (s, $\underline{C}_5Me_5$), 83.9 (d, $^1J_{CH}$ = 149.4 Hz, $C_1$), 44.8 (t, $^1J_{CH}$ = 127.8 Hz, $C_7$), 37.5 (t, $^1J_{CH}$ = 125.9 Hz, $CH_2$), 34.9 (t, $^1J_{CH}$ = 129.1 Hz, $CH_2$), 32.3 (t, $CH_2$), 32.1 (t, $CH_2$), 31.9 (t, $CH_2$), 30.4 (s, impurity, shows no CH correlation) 29.7 (t, $C_6$), 29.2 (t, $CH_2$), 28.6 (t, $CH_2$), 28.1 (t, $CH_2$), 27.4 (t, $CH_2$), 27.2 (t, $CH_2$), 27.0 (t, $CH_2$), 25.4 (t, $CH_2$), 9.0 (q, $^1J_{CH}$ = 128.7 Hz, $C_5\underline{Me}_5$); $^1H$-$^{13}C$ HETCORR (100 MHz, acetone-$d_6$, selected correlations only) $\delta$ 83.9 ($C_1$) $\leftrightarrow$ $\delta$ 4.30 ($H_1$); $\delta$ 44.8 ($C_7$) $\leftrightarrow$ $\delta$ 2.95 ($H_{7endo}$), $\delta$ 2.35 ($H_{7exo}$); $\delta$ 37.5 ($CH_2$) $\leftrightarrow$ $\delta$ 1.97 (strong correlation, $CH_2$); $\delta$ 34.9 ($CH_2$) $\leftrightarrow$ $\delta$ 2.85 ($CH_2$), $\delta$ 1.81 ($CH_2$); $\delta$ 32.3 ($CH_2$) $\leftrightarrow$ $\delta$ 2.20 ($CH_2$), $\delta$ 1.56 ($CH_2$); $\delta$ 32.1 ($CH_2$) $\leftrightarrow$ $\delta$ 1.87 (strong correlation, $CH_2$); $\delta$ 31.9 ($CH_2$) $\leftrightarrow$ $\delta$ 1.87 (strong correlation, $CH_2$); $\delta$ 29.7 ($C_6$) $\leftrightarrow$ $\delta$ 1.5 ($H_{6endo}$), $\delta$ -0.06 ($H_{6exo}$); $\delta$ 29.2 ($CH_2$) $\leftrightarrow$ $\delta$ 1.90 ($CH_2$), $\delta$ 1.55 ($CH_2$); $\delta$ 28.6 ($CH_2$) $\leftrightarrow$ $\delta$ 2.96 ($CH_2$), $\delta$ 2.69 ($CH_2$); $\delta$ 28.1 ($CH_2$) $\leftrightarrow$ $\delta$ 3.19 ($CH_2$), $\delta$ 2.94 ($CH_2$); $\delta$ 27.4 ($CH_2$) $\leftrightarrow$ $\delta$ 1.81 ($CH_2$), $\delta$ 1.31 ($CH_2$); $\delta$ 27.2 ($CH_2$) $\leftrightarrow$ $\delta$ 1.58 (strong correlation, $CH_2$); $\delta$ 27.0 ($CH_2$) $\leftrightarrow$ $\delta$ 1.58 ($CH_2$), $\delta$ 1.39 ($CH_2$); $\delta$ 25.4 ($CH_2$) $\leftrightarrow$ $\delta$ 1.79 ($CH_2$), $\delta$ 0.9 ($CH_2$); $\delta$ 9.0 ($C_5\underline{Me}_5$) $\leftrightarrow$ $\delta$ 1.75 ($C_5Me_5$). Analysis calculated for $C_{30}H_{44}CoF_3O_3S$: C, 59.99; H, 7.38; found: C, 59.949; H, 7.516.



**[(C$_5$Me$_5$)Co($\eta^5$-1-Ph-3,4-(CH$_2$)$_6$-C$_7$H$_6$)]$^+$ OTf$^-$ (98).** In the drybox, a Schlenk flask was charged with (C$_5$Me$_5$)Co($\eta^3$-C$_3$H$_5$)(OTf) (**80**) (58.7 mg, 0.153 mmol) and removed to the Schlenk line. Dichloromethane (6 mL) was added and the brown solution was cooled to -40 °C. Cyclooctyne (24 μL, 1.1 equiv) was added and the solution was stirred for about 6 min at -40 °C. Phenylacetylene (40 μL, 2.5 equiv) was then added, and the solution was allowed to warm to room temperature over 6 h and stirred an additional 2 h at room temperature. All volatile material was removed *in vacuo* and the residue was purified by flash chromatography (silica gel, 5% methanol/dichloromethane). A dark red band was collected and dried to give a dark red solid (57.5 mg, 63%). IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3059 (w), 2924 (m), 2854 (w), 1488 (w), 1478 (w), 1449 (m), 1381 (w), 1264 (s), 1222 (m), 1149 (s), 1110 (w), 1074 (m), 1030 (s), 769 (w), 734 (w), 699 (w), 637 (s), 571 (w), 517 (m); $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 7.55-7.40 (m, 5H, $H_{Ph}$), 5.79 (s, 1H, $H_4$), 4.20 (br s, 1H, $H_1$), 3.16 (dddd, $J$ = 16.0, 13.0, 7.0, 3.0 Hz, 1H, $H_{7endo}$), 3.02 (ddd, $J$ = 13.0, 13.0, 3.7 Hz, 1H, $CH_2$), 2.86 (ddd, $J$ = 13.2, 3.9, 3.9 Hz, 1H, $CH_2$), 2.67 (ddd, $J$ = 12.7, 12.7, 3.3 Hz, 1H, $CH_2$), 2.59 (ddd, $J$ = 16.7, 3.7, 3.7 Hz, 1H, $H_{7exo}$), 2.30-1.40[a] (series of overlapping m, $H_{6endo}$ and $CH_2$), 1.36 (s, 15H, C$_5$$\underline{\text{Me}}_5$), 0.35 (ddd, $J$ = 12.6, 12.6, 4.3 Hz, 1H, $H_{6exo}$). [a]The $H_{6endo}$ proton is identified at about δ 1.95 by the COSY spectrum. $^1$H-$^1$H COSY (400 MHz, $CD_2Cl_2$) δ 5.79 ($H_4$) ↔ δ 1.95 ($H_{6endo}$), δ 0.35 ($H_{6endo}$); δ 4.20 ($H_1$) ↔ δ 3.16 ($H_{7endo}$), δ 2.59 ($H_{7exo}$), δ 1.95 ($H_{6endo}$); δ 3.16 ($H_{7endo}$) ↔ δ 2.59 ($H_{7exo}$), δ 1.95 ($H_{6endo}$), δ 0.35 ($H_{6exo}$); δ 3.02 ($CH_2$) ↔ δ 2.86 ($CH_2$), δ 2.30 ($CH_2$), δ 1.80 ($CH_2$); δ 2.86 ($CH_2$) ↔ δ 2.30 ($CH_2$), δ 1.80 ($CH_2$); δ 2.67 ($CH_2$) ↔ δ 2.10 ($CH_2$), δ 1.70 ($CH_2$); δ 2.59 ($H_{7exo}$) ↔ δ 1.95 ($H_{6endo}$), δ 0.35 ($H_{6exo}$); δ 2.30-δ

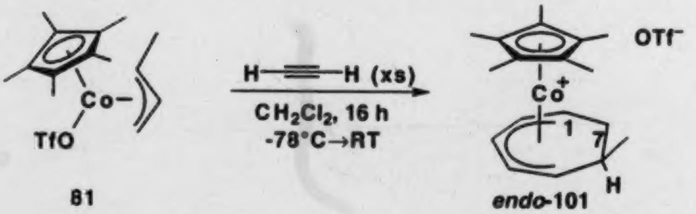
1.40 (series of correlations between $CH_2$ signals); δ 1.95 ($H_{6endo}$) ↔ δ 0.35 ($H_{6exo}$); $^{13}C$ NMR (100 MHz, $CD_2Cl_2$) δ 141.1 (s, $C_{Ph,\ ipso}$), 129.9[a] (d, $^1J_{CH}$ = 161.6 Hz, $C_{Ph}$), 129.8[a] (d, $^1J_{CH}$ = 161.6 Hz, $C_{Ph}$), 125.7[a] (d, $^1J_{CH}$ = 157.4 Hz, $C_{Ph}$), 108.6[b] (s, $C_{2/3/5}$), 107.7[b] (s, $C_{2/3/5}$), 97.5 (s, $C_5Me_5$), 90.9 (d, $^1J_{CH}$ = 162.7 Hz, $C_4$), 82.4 (d, $^1J_{CH}$ = 162.4 Hz, $C_1$), 48.7 (t, $^1J_{CH}$ = 127.2 Hz, $C_7$), 34.4 (t, $^1J_{CH}$ = 126.7 Hz, $CH_2$), 33.1[c] ($CH_2$), 32.1[c] ($C_6$), 31.5[c] ($CH_2$), 31.2[c] ($CH_2$), 26.72[d] (t, $^1J_{CH}$ = 130.8 Hz, $CH_2$), 26.65[d] (t, $^1J_{CH}$ = 130.8 Hz, $CH_2$), 8.8 (q, $^1J_{CH}$ = 128.8 Hz, $C_5Me_5$). [a] Signals overlap in gated decoupled spectrum. [b]One quaternary is not located. [c]Signals overlap in gated decoupled spectrum. *J* values are not available. [d]Signals overlap in gated spectrum. *J* value is obtained as an average value for the two signals. $^1H$-$^{13}C$ HETCORR (100 MHz, $CD_2Cl_2$) δ 129[a] ($C_{Ph}$) ↔ δ 7.45 ($H_{Ph}$); δ 125.7 ($C_{Ph}$) ↔ δ 7.45 ($H_{Ph}$); δ 90.9 ($C_4$) ↔ δ 5.79 ($H_4$); δ 82.4 ($C_1$) ↔ δ 4.20 ($H_1$); δ 48.7 ($C_7$) ↔ δ 3.16 ($H_{7endo}$), δ 2.59 ($H_{7exo}$); δ 34.4 ($CH_2$) ↔ δ 2.67 ($CH_2$), δ 1.85 ($CH_2$); δ 33.1 ($CH_2$) ↔ δ 3.02 ($CH_2$), δ 2.86 ($CH_2$); δ 32.1 ($C_6$) ↔ δ 1.95 ($H_{6endo}$), δ 0.35 ($H_{6exo}$); δ 31.5 ($CH_2$) ↔ δ 2.00 ($CH_2$), δ 1.65 ($CH_2$); δ 31.2 ($CH_2$) ↔ δ 2.15 ($CH_2$); δ 26.7[b] ($CH_2$) ↔ δ 1.75 ($CH_2$); δ 8.8 ($C_5\underline{Me_5}$) ↔ δ 1.36 ($C_5\underline{Me_5}$). [a]Unresolved signal consisting of δ 129.9 and δ 129.8. [b]Unresolved signal consisting of δ 26.72 and δ 26.65. Even after several recrystallizations from dichloromethane/diethyl ether and conversion to the $PF_6^-$ salt, the sample could not be obtained analytically pure. Electrospray MS *m/z* calculated for $C_{29}H_{38}Co$ ($M^+$- $OTf^-$): 445.230549; found: 445.230138 (100%). Analysis calculated for $C_{29}H_{38}CoF_6P$: C, 58.99; H, 6.49; found: C, 56.901; H, 6.401.



**80** **99**

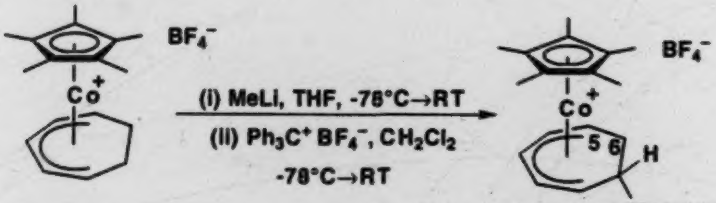
**$[(C_5Me_5)Co(\eta^5\text{-}C_7H_9)]^+ OTf^-$ (99).** In a Schlenk flask, $(C_5Me_5)Co(C_3H_5)(OTf)$ (**80**) (103.0 mg, 0.2680 mmol) was dissolved in distilled dichloromethane (15 mL) and cooled to -78 °C. Acetylene was bubbled through the solution for 15 min. The dark red solution was warmed slowly to room temperature and the solvent was removed *in vacuo*. Flash chromatography (4% methanol/dichloromethane, silica gel) gave a light orange compound (61.4 mg, 52%), which was homogenous by spectroscopic analysis. An analytical sample was prepared by careful chromatography followed by recrystallization from dichloromethane/diethyl ether. IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3052 (w), 2966 (w), 2924 (w), 2875 (w), 1599 (w), 1496 (m), 1474 (m), 1456 (m), 1434 (m), 1406 (w), 1380 (m), 1360 (w), 1340 (w), 1305 (w), 1269 (s), 1222 (m), 1189 (m), 1148 (s), 1078 (m), 1029 (s), 978 (w), 924 (w), 880 (m), 856 (w), 820 (w), 753 (w), 735 (w), 637 (s), 571 (m), 516 (m), 504 (m); $^1H$ NMR (400 MHz, $CD_2Cl_2$) $\delta$ 6.51 (apparent t, $J_{3\text{-}2} = J_{3\text{-}4} = 6.5$ Hz, 1H, $H_3$), 5.02 (apparent t, $J_{2\text{-}3} = 6.9$ Hz, $J_{2\text{-}1} = 8.6$ Hz, 2H, $H_{2/4}$), 4.42 (m, 2H, $H_{1/5}$), 2.28 (m, second order pattern, 2H, $H_{6endo/7endo}$), 1.83 (s, 15H, $C_5\underline{Me}_5$), 1.17 (m, second order pattern, 2H, $H_{6exo/7exo}$); $^1H$-$^1H$- COSY (400 MHz, $CD_2Cl_2$) $\delta$ 6.51 ($H_3$) $\leftrightarrow$ $\delta$ 5.02 ($H_{2,4}$); $\delta$ 4.42 ($H_{1,5}$) $\leftrightarrow$ $\delta$ 2.28 ($H_{6endo/7endo}$), $\delta$ 1.17 ($H_{6exo/7exo}$); $\delta$ 2.28 ($H_{6endo/7endo}$) $\leftrightarrow$ $\delta$ 1.17 ($H_{6endo/7endo}$); $^{13}C$ NMR (100 MHz, $CD_2Cl_2$) $\delta$ 121.1 (q, $^1J_{CF} = 321$ Hz, triflate carbon), 99.8 (d, $^1J_{CH} = 172$ Hz, $C_3$), 98.9 (s $\underline{C}_5Me_5$), 98.5 (d, $^1J_{CH} = 167.3$ Hz, $C_{2,4}$), 92.1 (dd, $^1J_{CH} = 154.8$ Hz, $^2J_{CH} = 8$ Hz, $C_{1/5}$), 34.2 (t, $^1J_{CH} = 132.5$ Hz, $C_{6/7}$), 9.7 (q, $^1J_{CH} = 129.0$ Hz, $C_5\underline{Me}_5$); $^1H$-$^{13}C$-HETCORR (100 MHz, $CD_2Cl_2$) $\delta$ 99.8 ($C_3$) $\leftrightarrow$ $\delta$ 6.51 ($H_3$); $\delta$ 98.5 ($C_{2/4}$) $\leftrightarrow$ $\delta$ 5.02 ($H_{2,4}$); $\delta$ 92.1 ($C_{1/5}$) $\leftrightarrow$ $\delta$ 4.42 ($H_{1/5}$); $\delta$ 34.2 ($C_{6/7}$) $\leftrightarrow$ $\delta$ 2.28 ($H_{6endo/7endo}$), $\delta$ 1.17 ($H_{6exo/7exo}$); $\delta$ 9.7 ($C_5\underline{Me}_5$) $\leftrightarrow$ $\delta$ 1.96 ($C_5\underline{Me}_5$). EMFAB-MS calculated for $C_{17}H_{24}Co$ ($M^+$ - OTf): 287.1210; found: 287.1214. Analysis calculated for $C_{18}H_{24}CoF_3O_3S$: C, 49.54; H, 5.54; S, 7.35; found: C, 49.973; H, 5.674; S, 7.041.

**[$(C_5Me_5)Co(\eta^5$-$C_7H_9)]^+BF_4^-$ (99-BF$_4$).** In the drybox, $(C_5Me_5)Co(C_2H_4)_2$ (**79**) (0.3103 g, 1.240 mmol) was placed in a Schlenk flask, and dissolved in hexane (10 mL), then the flask was removed to the Schlenk line, where cycloheptatriene (0.8 mL, excess) was added. The solution was heated to 60 °C for 18 h, then cooled back to room temperature. The cooled solution was filtered through a Celite pad and the volatile material was removed. The residue was redissolved in diethyl ether (20 mL) and cooled to -78 °C. Trifluoromethanesulfonic acid (109 μL, 1.0 equiv) was added, and the reaction was allowed to warm to room temperature over a 16 hour period. The orange brown precipitate was collected by filtration and washed with diethyl ether to give a light orange powder (0.377g, 70%). The compound was identical by $^1$H NMR spectroscopy to the triflate salt prepared by the reaction of allyl triflate **80** with acetylene.



**[$(C_5Me_5)Co(\eta^5$-6-Me-$C_7H_8)]^+$ OTf$^-$ (*endo*-101).** $(C_5Me_5)Co(\eta^3$-1-Me-$C_3H_4)(OTf)$ (**81**) (98.5 mg, 0.247 mmol) was dissolved in distilled dichloromethane (15 mL) and cooled to -78 °C. Acetylene was bubbled through the solution for 15 min and then the reaction was slowly warmed to room temperature. The solvent was removed *in vacuo* and the residue was purified by flash chromatography (4% methanol/dichloromethane, silica gel). The isolated yield of the orange solid was 88.5 mg (79%). An analytical sample was prepared by careful re-chromatography followed by recrystallization from dichloromethane/diethyl ether. IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3410 (w), 2966 (m), 2920 (m), 2876 (m), 1495 (m), 1459 (m), 1432 (m), 1408 (w), 1383 (m), 1368 (w), 1266 (s), 1222 (s), 1152 (s), 1078 (w), 1030 (s), 752 (w), 637 (s), 572 (m), 517 (m), 497 (w); $^1$H NMR (360 MHz, acetone-d$_6$) δ 6.73 (apparent t, $J_{3\text{-}2}$ = 6.8 Hz, $J_{3\text{-}4}$ = 7 Hz, 1H, H$_3$), 5.43

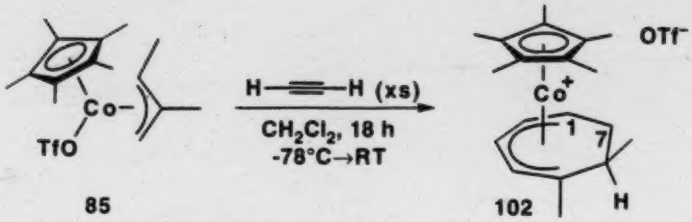
(apparent t, $J_{4\text{-}3}$ = 7 Hz, $J_{4\text{-}5}$ = 8.3 Hz, 1H, $H_4$), 5.13 (apparent t, $J_{2\text{-}3}$ = 6.8 Hz, $J_{2\text{-}1}$ = 9.0 Hz, 1H, $H_2$), 4.56 (ddd, $J_{1\text{-}2}$ = 9.2 Hz, $J_{1\text{-}7exo}$ = 3.9 Hz, $J_{1\text{-}7endo}$ = 1.2 Hz, 1H, $H_1$), 4.31 (ddd, $J_{5\text{-}4}$ = 7.9 Hz, $J_{5\text{-}6exo}$ = 3.8 Hz, $J_{5\text{-}7exo}$ = 1.2 Hz, 1H, $H_5$), 2.44 (ddd, $J_{7endo\text{-}7exo}$ = 16.4 Hz, $J_{7endo\text{-}6exo}$ = 8.7 Hz, $J_{7endo\text{-}1}$ = 1.2 Hz, 1H, $H_{7endo}$), 1.96 (s, 15H, $C_5\underline{Me_5}$), 1.95 (m, overlaps with $C_5Me_5$, 1H, $H_{7exo}$), 1.11 (d, $J$ = 6.7 Hz, 3H, $Me_6$), 0.97 (m, $J_{6exo\text{-}methyl}$ = 6.7 Hz, $J_{6exo\text{-}5}$ = 3.8 Hz, $J_{6exo\text{-}7endo}$ = 8.6 Hz, 1H, $H_{6exo}$); $^1$H-$^1$H COSY (360 MHz, acetone-$d_6$) δ 6.73 ($H_3$) ↔ δ 5.43 ($H_4$), δ 5.13 ($H_2$); δ 5.43 ($H_4$) ↔ δ 4.31 ($H_5$); δ 5.13 ($H_2$) ↔ δ 4.56 ($H_1$); δ 4.56 ($H_1$) ↔ δ 2.44 ($H_{7endo}$), δ 1.95 (w, $H_{7exo}$); δ 4.31 ($H_5$) ↔ δ 1.95 (w, $H_{7exo}$), δ 0.97 ($H_{6exo}$); δ 2.44 ($H_{7endo}$) ↔ δ 1.95 ($H_{7exo}$), δ 0.97 ($H_{6exo}$); δ 1.11 ($CH_3$) ↔ δ 0.97 ($H_{6exo}$); $^{13}$C NMR (100 MHz, acetone-$d_6$) δ 100.8 (dt, $^1J_{CH}$ = 172.6 Hz, $^2J_{CH}$ = 9 Hz, $C_3$), 99.4 (s, $\underline{C_5}Me_5$), 98.6$^a$ (d, $^1J_{CH}$ = 167.7 Hz, $C_2$), 98.3$^a$ (d, $^1J_{CH}$ = 163.0 Hz, $C_4$), 96.9$^a$ (d, $^1J_{CH}$ = 153.7 Hz, $C_5$), 89.7 (d, $^1J_{CH}$ = 154.3 Hz, $C_1$), 47.6 (t, $^1J_{CH}$ = 127.5 Hz, $C_7$), 36.6 (d, $^1J_{CH}$ = 125.0 Hz, $C_6$), 21.8 (q, $^1J_{CH}$ = 128.1 Hz, $Me_6$), 9.4 (q, $^1J_{CH}$ = 128.8 Hz, $C_5\underline{Me_5}$). $^a$Overlapping peaks in gated spectrum; $^1J_{CH}$ values are approximate. $^1$H-$^{13}$C HETCORR (100 MHz, $CD_2Cl_2$) δ 100.8 ($C_3$) ↔ δ 6.73 ($H_3$); δ 98.6 ($C_2$) ↔ δ 5.13 ($H_2$); δ 98.3 ($C_4$) ↔ δ 5.43 ($H_4$); δ 96.9 ($C_5$) ↔ δ 4.31 ($H_5$); δ 89.7 ($C_1$) ↔ δ 4.56 ($H_1$); δ 47.6 ($C_7$) ↔ δ 2.44 ($H_{7endo}$), δ 1.95 ($H_{7exo}$); δ 36.6 ($C_6$) ↔ δ 0.97 ($H_{6exo}$); δ 21.8 (Me) ↔ δ 1.11 (Me); δ 9.4 ($C_5\underline{Me_5}$) ↔ δ 1.96 ($C_5\underline{Me_5}$). EMFAB MS calculated for $C_{18}H_{26}Co$ ($M^+$ - OTf): 301.1366, found: 301.1372. Analysis calculated for $C_{19}H_{26}CoF_3O_3S$: C, 50.67; H, 5.82; found: C, 50.710 H, 5.761.



99

*exo*-101

**[(C$_5$Me$_5$)Co($\eta^5$-6-Me-C$_7$H$_8$)]$^+$ OTf$^-$ (*exo*-101).** To a slurry of (C$_5$Me$_5$)Co($\eta^5$-C$_7$H$_9$) (**99**) (0.1268 g, 0.3389 mmol) in THF (10 mL) at -78°C was added MeLi ( 1.4 M, THF/cumene, 1.5 equiv, 0.36 mL). The reaction was allowed to warm slowly to room temperature over 16h, resulting in a light orange solution. The solvent was removed *in vacuo* and the residue was extracted with pentane in the drybox. The pentane extracts were filtered through a Celite pad and the pentane was removed. The residue was dissolved in dichloromethane and cooled to -78°C. Trityl tetrafluoroborate (175.3 mg, 1.6 equiv) was added, causing an immediate color change from light orange to dark red. The solution was stirred at -78°C for 30 min, then the cooling bath was removed and the solution was allowed to warm to room temperature and stirred at that temperature for 30 min. The solvent volume was reduced to about 2 mL and the product was precipitated with diethyl ether. The orange product was again recrystallized from dichloromethane/diethyl ether to give an orange powder (0.042 g, 32%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.67 (ddd, $J_{3\text{-}2}$ = 6.9 Hz, $J_{3\text{-}4}$ = 6.1 Hz, $J_{3\text{-}5}$ = 1.3 Hz, 1H, H$_3$), 5.36 (dd, $J_{4\text{-}5}$ = 7.9 Hz, $J_{4\text{-}3}$ = 6.1 Hz, 1H, H$_4$), 4.84 (dd, $J_{2\text{-}1}$ = 9.0 Hz, $J_{2\text{-}3}$ = 6.9 Hz, 1H, H$_2$), 4.30 (ddd, $J_{1\text{-}2}$ = 9.3 Hz, $J_{1\text{-}7\text{endo}}$ = 3.7 Hz, $J_{1\text{-}6\text{endo}}$ = 1.7 Hz, 1H, H$_1$), 4.22 (dddd, $J_{5\text{-}4}$ = $J_{5\text{-}6\text{endo}}$ = 8.0 Hz, $J_{5\text{-}6\text{exo}}$ = 5.3 Hz, $J_{5\text{-}3}$ = 1.3 Hz, 1H, H$_5$), 3.13 (m, dddq by decoupling, $J_{7\text{endo-}6\text{exo}}$ = 10.4 Hz, $J_{7\text{endo-}6\text{endo}}$ = 8.0 Hz, $J_{7\text{endo-}1}$ = 3.8 Hz, $J_{7\text{endo-Me}}$ = 6.7 Hz, 1H, H$_{7\text{endo}}$), 1.83 (s, 15H, C$_5$Me$_5$), 1.80 (m, obscured by C$_5$Me$_5$, 1H, H$_{6\text{endo}}$), 0.86 (d, $J_{\text{Me-}7}$ = 6.7 Hz, 3H, Me), -0.19 (ddd, $J_{6\text{exo-}6\text{endo}}$ = 13.2 Hz, $J_{6\text{exo-}7}$ = 10.5 Hz, $J_{6\text{exo-}5}$ = 4.8 Hz, 1H, H$_{6\text{exo}}$); $^1$H-$^1$H GCOSY (300 MHz, CDCl$_3$) $\delta$ 6.67 (H$_3$) $\leftrightarrow$ $\delta$ 5.36 (H$_4$), $\delta$ 4.84 (H$_2$), $\delta$ 4.22 (w, H$_5$); $\delta$ 5.36 (H$_4$) $\leftrightarrow$ $\delta$ 4.22 (H$_5$); $\delta$ 4.84 (H$_2$) $\leftrightarrow$ $\delta$ 4.30 (H$_1$); $\delta$ 4.30 (H$_1$) $\leftrightarrow$ $\delta$ 3.13 (H$_{7\text{endo}}$); $\delta$ 4.22 (H$_5$) $\leftrightarrow$ $\delta$ 1.80 (H$_{6\text{endo}}$), $\delta$ -0.19 (H$_{6\text{exo}}$); $\delta$ 3.13 (H$_{7\text{endo}}$) $\leftrightarrow$ $\delta$ 1.80 (H$_{6\text{endo}}$), $\delta$ 0.86 (CH$_3$), $\delta$ -0.19 (H$_{6\text{exo}}$); $\delta$ 1.80 (H$_{6\text{endo}}$) $\leftrightarrow$ $\delta$ -0.19 (H$_{6\text{exo}}$).

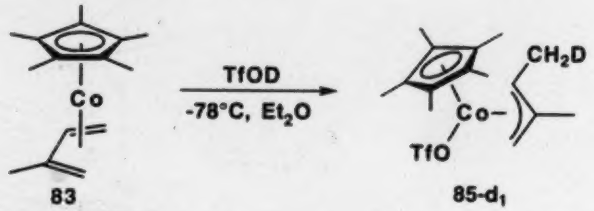


85

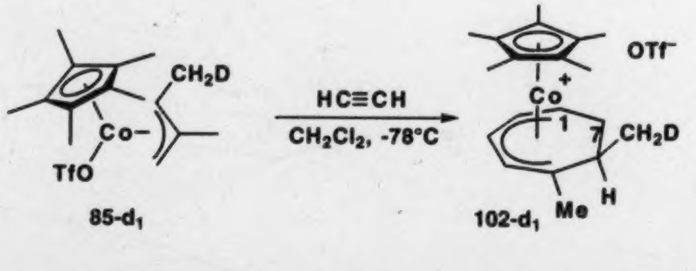
102

**$[(C_5Me_5)Co(\eta^5\text{-}5,6\text{-}Me_2C_7H_7)]^+ OTf^-$ (102).** $(C_5Me_5)Co(\eta^3\text{-}1,2\text{-}Me_2\text{-}C_3H_3)(OTf)$ (**85**) (83.2 mg, 0.202 mmol) was dissolved in distilled dichloromethane (15 mL) under an inert atmosphere and cooled to -78 °C. Acetylene was then bubbled through the red-brown solution for about 15 min. The dark orange-red solution was then warmed to room temperature over 18 h. Removal of the solvent *in vacuo* was followed by flash chromatography (4% methanol/dichloromethane, silica gel) to give a red solid (62.8 mg, 67%). Additional impure fractions were recovered, for a total approximate yield of 80%. An analytical sample was prepared by recrystallization from dichloromethane/diethyl ether. IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3405 (w), 2967 (w), 2915 (w), 2876 (w), 1455 (w), 1433 (w), 1382 (w), 1267 (s), 1223 (m), 1146 (s), 1075 (w), 1047 (w), 1031 (s), 637 (s), 572 (w), 517 (w); $^1H$ NMR (400 MHz, acetone-$d_6$) δ 6.67 (apparent t, $J_{3\text{-}2}$ = 6.5 Hz, $J_{3\text{-}4}$ = 6.2 Hz, 1H, $H_3$), 5.34 (d, $J_{4\text{-}3}$ = 6.5 Hz, 1H, $H_4$), 5.00 (apparent t, $J_{2\text{-}1}$ = 8.8 Hz, $J_{2\text{-}3}$ = 6.7 Hz, 1H, $H_2$), 4.46 (ddd, $J_{1\text{-}2}$ = 8.7 Hz, $J_{1\text{-}7exo}$ = $J_{1\text{-}7endo}$ = 4.4 Hz, 1H, $H_1$), 2.41 (ddd, $J_{7endo\text{-}7exo}$ = 16 Hz, $J_{7endo\text{-}6exo}$ = 8.8 Hz, $J_{7endo\text{-}1}$ = 4.4 Hz, 1H, $H_{7endo}$), 1.88 (s, 15H, $C_5\underline{Me_5}$), 1.8 (m, overlaps with $C_5\underline{Me_5}$, 1H, $H_{7exo}$), 1.55 (s, 3H, $Me_5$), 1.05 (d, $J_{Me\text{-}6}$ = 6.8 Hz, 3H, $Me_6$), 0.90 (m, $J_{6\text{-}Me}$ = 6.7 Hz, $J_{6\text{-}7endo}$ = 8.8 Hz, 1H, $H_6$); $^1H$-$^1H$ COSY (400 MHz, acetone-$d_6$) δ 6.76 ($H_3$) ↔ δ 5.34 ($H_4$), δ 5.00 ($H_2$), δ 1.55 (w, $Me_5$); δ 5.34 ($H_4$) ↔ δ 5.00 ($H_2$), δ 1.55 ($Me_5$); δ 5.00 ($H_2$) ↔ δ 4.46 ($H_1$), δ 1.8 ($H_{7exo}$); δ 4.46 ($H_1$) ↔ δ 2.41 ($H_{7endo}$), δ 1.8 ($H_{7exo}$); δ 2.41 ($H_{7endo}$) ↔ δ 1.8 ($H_{7exo}$), δ 0.90 ($H_{6exo}$); δ 1.55 ($Me_5$) ↔ δ 0.90 (w, $H_{6exo}$); δ 1.05 ($Me_6$) ↔ δ 0.90 ($H_{6exo}$); $^{13}C$ NMR (100 MHz, $CD_2Cl_2$) δ 114.9 (s, $C_5$), 97.9 (d, $^1J_{CH}$ = 167.5 Hz, $C_4$), 97.5 (d, $^1J_{CH}$ = 168 Hz, $C_2$), 97.8 (s, $\underline{C}_5Me_5$), 96.7 (dd, $^1J_{CH}$ = 163 Hz, $^2J_{CH}$ = 9.1 Hz, $C_3$), 84.9 (d, $^1J_{CH}$ = 154.0 Hz,

$C_1$), 47.2 (t, $^1J_{CH}$ = 129 Hz, $C_7$), 40.4 (d, $^1J_{CH}$ = 129.6 Hz, $C_6$), 23.5 (q, $^1J_{CH}$ = 127.9 Hz, $Me_5$), 17.9 (q, $^1J_{CH}$ = 127.2 Hz, $Me_6$), 9.3 (q, $^1J_{CH}$ = 128.8 Hz, $C_5\underline{Me}_5$); $^1$H-$^{13}$C HETCORR (100 MHz, $CD_2Cl_2$) δ 97.9 ($C_4$) ↔ δ 5.34 ($H_4$); δ 97.5 ($C_2$) ↔ δ 5.00 ($H_2$); δ 96.7 ($C_3$) ↔ δ 6.67 ($H_3$); δ 84.9 ($C_1$) ↔ δ 4.46 ($H_1$); δ 47.2 ($C_7$) ↔ δ 2.41 ($H_{7endo}$), δ 1.8 ($H_{7exo}$); δ 40.4 ($C_6$) ↔ δ 0.90 ($H_6$); δ 23.5 ($Me_5$) ↔ δ 1.55 ($Me_5$); δ 17.9 ($Me_6$) ↔ δ 1.05 ($Me_6$); δ 9.3 ($C_5\underline{Me}_5$) ↔ δ 1.88 ($C_5\underline{Me}_5$). EMFAB MS calculated for $C_{19}H_{28}Co$ ($M^+$ - $OTf^-$): 315.1523; found: 315.1525. Analysis calculated for $C_{20}H_{26}CoF_3O_3S$: C, 51.95; H, 5.67; found: C, 51.583; H, 6.127.

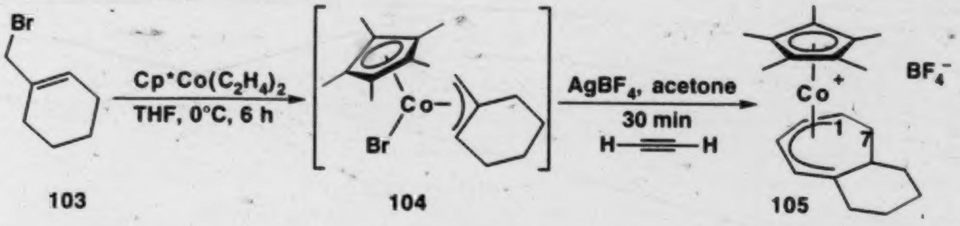


**($C_5Me_5$)Co($\eta^3$-1-($CH_2D$)-2-Me-$C_3H_3$)(OTf) (85-d$_1$).** This compound was prepared by the procedure for the unlabelled analogue[88,89] with the following exceptions. Neat DOTf was used, instead of a solution of HOTf in diethyl ether. After the reaction was allowed to warm to room temperature, the solvent was removed by cannula transfer and the dark brown solid was washed with diethyl ether and dried. The solid was then used without further purification or characterization.

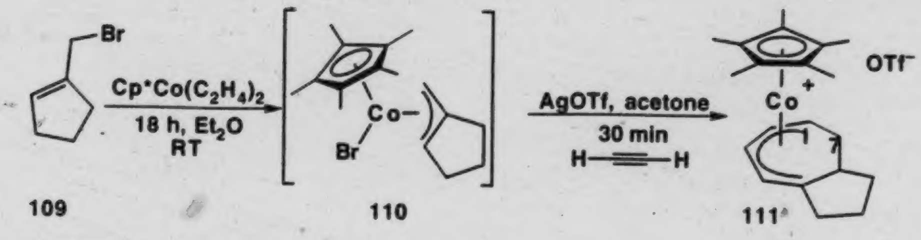


**[($C_5Me_5$)Co($\eta^5$-5-Me-6-($CH_2D$)-$C_7H_7$)]$^+$ $OTf^-$ (102-d$_1$).** This compound was prepared by following the procedure for the unlabelled analogue. $^1$H NMR (400 MHz, $CDCl_3$) identical to the unlabelled compound except for δ 1.0 (m, 2H, $C\underline{H}_2D$). $^2$H NMR (76.7

MHz, $CHCl_3$) δ 1.02 (s, $C\underline{D}H_2$). The deuterium label was not observed above the baseline in the IR spectrum.



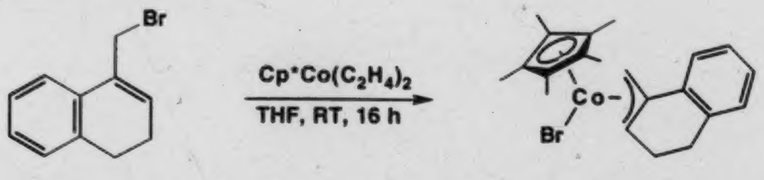
**[($C_5Me_5$)Co($\eta^5$-bicyclo[5.4.0]undeca-1,3-dien-5-yl)]$^+$ $BF_4^-$ (105).** A solution of ($C_5Me_5$)Co($C_2H_4$)$_2$ (**79**) (0.3261 g, 1.303 mmol) in tetrahydrofuran (20 mL) was prepared and cooled briefly to 0 °C under nitrogen. 2-bromo-1-methylenecyclohexane (**103**) (165 µL, 1.1 equiv) was added and the solution stirred for 6 h at room temperature. The solvent was then removed *in vacuo*, and the residue dissolved in reagent acetone (20 mL). $AgBF_4$ (0.257 g, 1.2 equiv) was added and acetylene was bubbled into the solution for 3 min. The flask was sealed, and the solution was stirred 30 min. Solid residue was removed by filtration and the solvent was removed. The residue was chromatographed on silica gel using 7% methanol/dichloromethane. The red fraction was collected and dried. Recrystallization from dichloromethane/diethyl ether gave a deep red solid (0.327 g, 59%). NMR spectra were obtained in two different solvents to help distinguish overlapping signals. IR ($CH_2Cl_2$ cast, cm$^{-1}$) 2940 (m), 2090 (m), 2867 (m), 1489 (w), 1461 (m), 1430 (w), 1389 (m), 1055 (vs), 1036 (m), 519 (w); $^1H$ NMR (300 MHz, $CD_2Cl_2$) δ 6.49 (t, $J$ = 6.4 Hz, 1H, $H_3$), 5.14 (d, $J$ = 5.8 Hz, 1H, $H_4$), 4.62 (t, $J$ = 8 Hz, 1H, $H_2$), 4.3-4.2 (m, 1H, $H_1$), 2.50 (ddd, $J$ = 17, 10.6, 3.1 Hz, 1H, $H_{7endo}$), 2.23 (br d, $J$ = 17 Hz, 1H, $H_{7exo}$), 2.1-1.0 (series of m, cyclohexane ring), 1.77 (s, 15H, $C_5\underline{Me_5}$), 0.4-0.3 (m, 1H, $H_6$); $^1H$-$^1H$ COSY DQF (400 MHz, $CD_2Cl_2$) δ 6.49 ($H_3$) ↔ δ 5.14 ($H_4$), δ 4.62 ($H_2$); δ 4.25 ($H_1$) ↔ δ 2.50 ($H_{7endo}$), δ 2.23 ($H_{7exo}$); δ 2.50 ($H_{7endo}$) ↔ δ 2.23 ($H_{7exo}$); $^{13}C$ NMR (100 MHz, $CD_2Cl_2$) δ 118.7 (s, $C_5$), 97.9[a] (d, $J$ = 178 Hz, $C_{4/3/2}$), 97.1[a] (d, $J$ = 178 Hz, $C_{4/3/2}$), 97.0 (s, $\underline{C}_5Me_5$), 86.6 (d, $^1J_{CH}$ = 149.0 Hz, $C_1$), 49.9 (t, $^1J_{CH}$ = 129.9 Hz, $C_7$), 39.9 (d, $^1J_{CH}$ = 133.1 Hz, $C_6$), 31.3 (t, $^1J_{CH}$ = 128.5 Hz, $CH_2$), 27.0 (t, $^1J_{CH}$ = 122.8 Hz, $CH_2$), 22.3 (t, $^1J_{CH}$ = 128.2 Hz, $CH_2$), 19.3 (t, $^1J_{CH}$ = 125.3 Hz, $CH_2$), 9.5 (q, $^1J_{CH}$ = 128.7 Hz, $C_5\underline{Me_5}$). [a] These carbons overlap in the gated spectrum, so only a broad signal is seen. $^1H$-$^{13}C$ HETCORR (100 MHz, $CD_2Cl_2$) δ 97.5 ($C_{4/3/2}$)[a] ↔ δ 6.49 ($H_3$), δ 5.14 ($H_4$), δ 4.62 ($H_1$); δ 86.6 ($C_1$) ↔ δ 4.25 ($H_1$); δ 49.9 ($C_7$) ↔ δ 2.50[b] ($H_{7endo}$); δ 39.9 ($C_6$) ↔ δ 0.35 ($H_6$); δ 31.3 ($CH_2$) ↔ δ 2.05 ($CH_2$), δ 1.45 ($CH_2$); δ 27.0 ($CH_2$) ↔ δ 1.40 ($CH_2$); δ 22.3 ($CH_2$) ↔ δ 1.80 ($CH_2$), δ 1.55 ($CH_2$); δ 19.3 ($CH_2$) ↔ δ 1.65 ($CH_2$), δ 1.15 ($CH_2$); δ 9.5 ($C_5\underline{Me_5}$) ↔ δ 1.77 ($C_5\underline{Me_5}$). [a]The resolution is insufficient to assign specific carbons. [b]This correlation is broad enough to also correlate to δ 2.23 ($H_{7exo}$), although only one (large) cross peak is seen in the spectrum. $^1H$ NMR (360 MHz, acetone-$d_6$) δ 6.69 (dd, $J_{3\text{-}4}$ = 6.1 Hz, $J_{3\text{-}2}$ = 7.1 Hz, 1H, $H_3$), 5.44 (d, $J_{4\text{-}3}$ = 6.1 Hz, 1H, $H_4$), 4.86 (br t, $J$ = 8 Hz, ddd by decoupling, $J_{2\text{-}1}$ = 9.2 Hz, $J_{2\text{-}3}$ = 7.1 Hz, $J_{2\text{-}7exo}$= 1.3 Hz, 1H, $H_2$), 4.47 (dtd, $J_{1\text{-}2}$ = 9.2 Hz, $J_{1\text{-}7exo}$ = $J_{1\text{-}7endo}$ = 3.6 Hz, $J_{1\text{-}3}$ < 1Hz, 1H, $H_1$), 2.66 (ddd, $J_{7endo\text{-}7exo}$ = 17.1 Hz, $J_{7endo\text{-}6}$ = 10.8 Hz, $J_{7endo\text{-}1}$ = 3.6 Hz, 1H, $H_{7endo}$), 2.26 (m, dddd by decoupling, $J_{7exo\text{-}7endo}$ = 17.1 Hz, $J_{7exo\text{-}6}$ = 4.8 Hz, $J_{7exo\text{-}1}$ = 3.6 Hz, $J_{7exo\text{-}2}$ = 1.3 Hz, 1H, $H_{7exo}$), 2.20 (ddd, $J$ = 12, 12, 6, 1H, $H_8$), 2.0-1.0 (series of m, 7H, $CH_2$), 1.85 (s, 15H, $C_5\underline{Me_5}$), 0.38 (dddd, $J_{6\text{-}8a}$ = $J_{6\text{-}7endo}$ = 10.8 Hz, $J_{6\text{-}7exo}$ ≈ $J_{6\text{-}8s}$ = 4.8 Hz, 1H, $H_6$); HMQC (300 MHz, acetone-$d_6$, select data only) δ 97[a]($C_{4/3/2}$) ↔ δ 6.69 ($H_3$), δ 5.44 ($H_4$), δ 4.86 ($H_2$); δ 86.6 ($C_1$) ↔ δ 4.47 ($H_1$); δ 49.9 ($C_7$) ↔ δ 2.66 ($H_{7endo}$), δ 2.26 ($H_{7exo}$); δ 39.9 ($C_6$) ↔ δ 0.38 ($H_6$). [a]These carbon signals overlap. HMBC (300 MHz, acetone-$d_6$) δ 118.7 ($C_5$) ↔ δ 6.69 ($H_3$), δ 2.20 ($CH_2$); δ 97[a]($C_{4/3/2}$) ↔ δ 6.69 ($H_3$), δ 5.44 ($H_4$), δ 4.86 ($H_2$), δ 4.47 ($H_1$), δ 2.66 ($H_{7endo}$), δ 2.26 ($H_{7exo}$), δ 2.20 ($CH_2$); δ 86.6 ($C_1$) ↔ δ 6.69 ($H_3$), δ 2.66 ($H_{7endo}$), δ 2.20 ($H_{7exo}$); δ 49.9 ($C_7$) ↔ δ 4.86 ($H_2$), δ 1.5 ($CH_2$); δ 39.9 ($C_6$) ↔ δ 5.44 ($H_4$), δ 4.47 ($H_1$), δ 2.66 ($H_{7endo}$), δ 2.26 ($H_{7exo}$), δ 1.8-1.5[b]; δ 31.3 ($CH_2$) ↔ δ 5.44 ($H_4$); δ 27.0 ($CH_2$) ↔ δ 2.66 ($H_{7exo}$). [a] These carbon signals overlap. [b] Shows correlations to several $CH_2$ signals. Analysis calculated for $C_{21}H_{30}BCoF_4$: C, 58.90; H, 7.06; found: C, 58.602; H, 7.063.



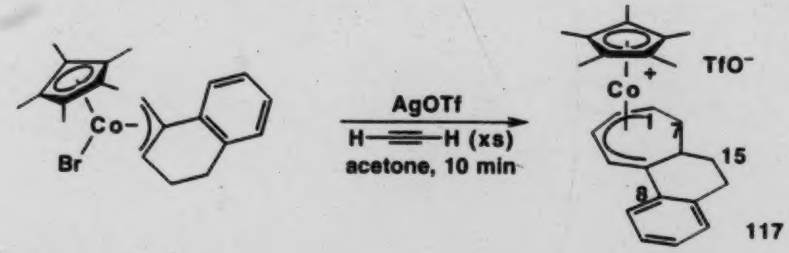
**$[(C_5Me_5)Co(\eta^5$-bicyclo[5.3.0]deca-1,3-dien-5-yl)$]^+$ $OTf^-$ (111).** A solution of $(C_5Me_5)Co(C_2H_4)_2$ (**79**) (0.1708 g, 0.6824 mmol) in diethyl ether (30 mL) was prepared. The solution was cooled briefly to 0 °C under nitrogen. 1-(bromomethyl)-1-cyclopentene (**109**) (165 µL, 1.5 equiv) was added and the solution stirred for 18 h at room temperature to give a deep purple solution. The solution was filtered under nitrogen through Celite, rinsed with diethyl ether (20 mL) and the solvent was then removed *in vacuo*. Complex **110** can be isolated at this point if so desired and used in other reactions. The residue was dissolved in reagent acetone (20 mL). AgOTf (0.2029 g, 1.16 equiv) was added, and acetylene was bubbled into the solution for 3 min. The flask was sealed, and the solution was stirred 30 min. After filtration to remove silver residues, the solvent was removed and the residue was chromatographed on silica gel using 5% methanol/dichloromethane. The red fraction was collected and dried to give an orange-red solid (0.154 g, 47%). This procedure was repeated using $AgBF_4$, which gave a more crystalline material. This material was recrystallized from dichloromethane/diethyl ether to give the analytical sample. Crystals suitable for X-ray diffraction analysis were grown by layering diethyl ether on top of a concentrated solution of the $BF_4^-$ salt in dichloromethane. For full data on this crystal structure, request report # JMS9711 from the Structure Determination Laboratory at the University of Alberta Department of Chemistry. IR ($CH_2Cl_2$ cast, $cm^{-1}$) 2955 (w), 2904 (w), 2867 (w), 2826 (w), 1470 (w), 1455 (w), 1429 (w), 1388 (m), 1281 (w), 1053 (s), 1036 (s), 949 (w), 919 (w), 886 (w), 842 (m), 824 (w), 732 (w), 715 (w), 521 (w); $^1H$ NMR (300 MHz, $CDCl_3$) δ 6.55 (apparent t, $J_{3\text{-}4}$ = 6.0 Hz, $J_{3\text{-}2}$ = 7.2 Hz, 1H, $H_3$), 5.39 (d, $J_{4\text{-}3}$ = 6.0 Hz, 1H, $H_4$), 4.66 (apparent t, $J_{2\text{-}1}$ = $J_{2\text{-}3}$ = 8.4 Hz, 1H,

$H_2$), 4.18 (dt, $J_{1\text{-}2}$ = 9.6 Hz, $J_{1\text{-}7exo}$ = $J_{1\text{-}7endo}$ = 3.5 Hz, 1H, $H_1$), 2.46 (ddd, $J_{7endo\text{-}7exo}$ = 17.4 Hz, $J_{7endo\text{-}6}$ = 10.2 Hz, $J_{7endo\text{-}1}$ = 3.6 Hz, 1H, $H_{7endo}$), 2.34 (ddd, $J_{7exo\text{-}7endo}$ = 17.1 Hz, $J_{7exo\text{-}6}$ = $J_{7exo\text{-}1}$ = 4.2 Hz, 1H, $H_{7exo}$), 2.0-1.8 (m, 4H, $CH_2$), 1.79 (s, 15H, $C_5\underline{Me_5}$), 1.3-1.1 (m, 2H, $CH_2$), 0.62-0.52 (m, 1H, $H_6$); $^1H$-$^1H$ GCOSY (300 MHz, $CDCl_3$) δ 6.55 ($H_3$) ↔ δ 5.39 ($H_4$), δ 4.18 ($H_2$); δ 4.66 ($H_2$) ↔ δ 4.18 ($H_1$); δ 4.18 ($H_1$) ↔ δ 2.46 ($H_{7endo}$), δ 2.34 ($H_{7exo}$); δ 2.46 ($H_{7endo}$) ↔ δ 0.6 ($H_6$); δ 2.34 ($H_{7exo}$) ↔ δ 0.6 ($H_6$); δ 1.9 ($CH_2$) ↔ δ 1.2 ($CH_2$), δ 0.6 ($H_6$); δ 1.2 ($CH_2$) ↔ δ 0.6 ($H_6$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 119.2 (s, $C_5$), 97.5 (s, $\underline{C_5}Me_5$), 97.3 (dt, $^1J_{CH}$ = 166.4 Hz, $^2J_{CH}$ = 7.5 Hz, $C_2$), 96.4[a] (dd, $^1J_{CH}$ = 169 Hz, $^2J_{CH}$ = 9.2 Hz, $C_3$), 94.5 (d, $^1J_{CH}$ = 165.6 Hz, $C_4$), 86.7 (d, $^1J_{CH}$ = 152.0 Hz, $C_1$), 48.8 (t, $^1J_{CH}$ = 126.9 Hz, $C_7$), 42.3 (d, $^1J_{CH}$ = 130.3 Hz, $C_6$), 36.3 (t, $^1J_{CH}$ = 127.6 Hz, $CH_2$), 33.0 (t, $^1J_{CH}$ = 132.2 Hz, $CH_2$), 26.8 (t, $^1J_{CH}$ = 132.2 Hz, $CH_2$), 9.2 (q, $^1J_{CH}$ = 128.7 Hz, $C_5\underline{Me_5}$). [a] This signal overlaps with the $\underline{C_5}Me_5$ signal in the gated decoupled spectrum. HMQC (300 MHz, $CDCl_3$) δ 97.3 ($C_2$) ↔ δ 4.66 ($H_2$); δ 96.4 ($C_3$) ↔ δ 6.55 ($H_3$); δ 94.5 ($C_4$) ↔ δ 5.39 ($H_4$); δ 86.7 ($C_1$) ↔ δ 4.18 ($H_1$); δ 48.8 ($C_7$) ↔ δ 2.46 ($H_{7endo}$), δ 2.34 ($H_{7exo}$); δ 42.3 ($C_6$) ↔ δ 0.57 ($H_6$); δ 36.3 ($CH_2$) ↔ δ 1.8 ($CH_2$); δ 33.0 ($CH_2$) ↔ δ 1.2 ($CH_2$); δ 26.8 ($CH_2$) ↔ δ 1.7 ($CH_2$); δ 9.2 ($C_5\underline{Me_5}$) ↔ δ 1.79 ($C_5\underline{Me_5}$). As mentioned, the analytical sample was prepared using $AgBF_4$ instead of AgOTf. This substitution did not significantly change the appearance of the NMR spectra and allowed more facile purification of the product. Analysis calculated for $C_{20}H_{28}BCoF_4$: C, 58.00; H, 6.81; found: C, 57.639; H, 7.017.

**1-(Bromomethyl)-3,4-dihydronaphthalene (116)**. A solution of 1-(hydroxymethyl)-3,4-dihydronaphthalene (**115**)[114b,c] (0.440 g, 2.75 mmol) in diethyl ether (50 mL) was cooled to -78°C and $PBr_3$ (0.740 g, 2.75 mmol) was added dropwise. The solution was allowed to warm to room temperature overnight. To the solution was added water (20 mL) and the organic layer was separated. The organic layer was then washed with a saturated solution of $NaHCO_3$ (2x5 mL) and dried ($Na_2SO_4$). The diethyl ether was removed by rotary evaporation, leaving a colorless oily residue (0.220 g, 36%). This material was characterized by $^1$H NMR spectroscopy and used directly in the next step. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.42 (d, $J$ = 7.5 Hz, 1H, $H_{Ph}$), 7.29-7.15 (m, 3H, $H_{Ph}$), 6.28 (t, $J$ = 4.5 Hz, 1H, $H_2$), 4.37 (s, 2H, $C\underline{H}_2Br$), 2.80 (t, $J$ = 7.8 Hz, 2H, $H_4$), 2.34 (td, $J$ = 8.4, 4.8 Hz, 2H, $H_3$).

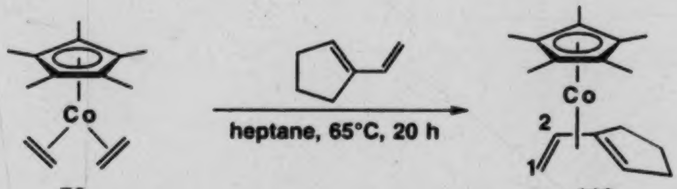


**$(C_5Me_5)Co(\eta^3\text{-}C_{11}H_{11})(Br)$.** To a solution of $(C_5Me_5)Co(C_2H_4)_2$ (**79**) (0.1746g, 0.698 mmol) in THF (5 mL) was added a solution of 1-(bromomethyl)-3,4-dihydronaphthalene (**116**) (0.154 g, 0.693 mmol, 1 equiv) in THF (about 7 mL). The solution was stirred at room temperature overnight, after which all volatile material was removed *in vacuo*. The residue was extracted with toluene until no more colored material could be dissolved. The toluene solution was then filtered through a Celite pad and reduced to dryness. A dark purple-red residue (0.2396 g, 82%) was left. This material was used directly in the next step without further purification.



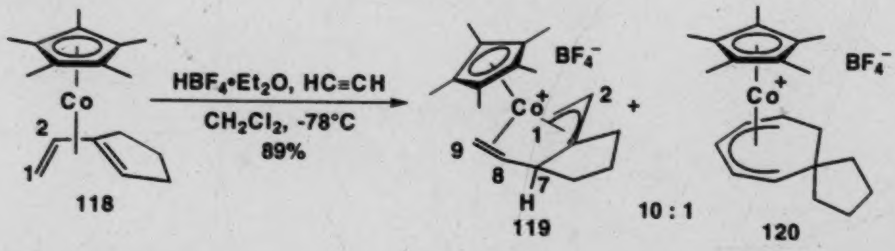
**$[(C_5Me_5)Co(\eta^5\text{-}5,6\text{-}(C_8H_8)\text{-}C_7H_7)]^+ OTf^-$ (117).** In the drybox, $(C_5Me_5)Co(C_{11}H_{11})(Br)$ (62.9 mg, 0.151 mmol) was weighed into a Schlenk flask and removed to the Schlenk line, where degassed acetone (15 mL) was added, followed by silver triflate (62.1 mg, 2.26 mmol, 1.5 equiv). The mixture was stirred for 1 min, then acetylene was bubbled into the solution. After 10 min, the suspension was filtered to remove silver residues and the solvent was removed. The crude product was purified by flash chromatography on silica gel, using 5% methanol/dichloromethane as the eluent. Evaporation of the dark red band gave a red-black solid (32 mg, 44%). IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3061 (m), 2927 (m), 1679 (w), 1600 (w), 1455 (m), 1383 (m), 1262 (s), 1224 (s), 1155 (s), 1074 (m), 1030 (s), 869 (w), 767 (m), 735 (m), 701 (m), 638 (s), 573 (m), 517 (m); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.47 (d, $J$ = 7.5 Hz, 1H, $H_9$), 7.30-7.20 (m, 2H, $H_{11/10}$), 7.16 (d, $J$ = 6.9 Hz, 1H, $H_{12}$), 7.04 (dd, $J_{3\text{-}2}$ = 7.1 Hz, $J_{3\text{-}4}$ = 6.6 Hz, 1H, $H_3$), 6.51 (d, $J_{4\text{-}3}$ = 6.6 Hz, 1H, $H_4$), 4.88 (dd, $J_{1\text{-}2}$ = 9.6 Hz, $J_{2\text{-}3}$ = 7.3 Hz, 1H, $H_2$), 4.41 (m, ddd by decoupling, $J_{1\text{-}2}$ = 9.1 Hz, $J_{1\text{-}7exo} \approx J_{1\text{-}7endo} \approx$ 3.0 Hz, 1H, $H_1$), 2.90 (ddd, $J_{7endo\text{-}7exo}$ = 17.0 Hz, $J_{7endo\text{-}6}$ = 11.3 Hz, $J_{7endo\text{-}1}$ = 3.3 Hz, 1H, $H_{7endo}$), 2.65-2.55 (m, 2H, $H_{14}$), 2.12 (br d, $J$ = 17 Hz, dddd by decoupling, $J_{7exo\text{-}7endo}$ = 17 Hz, $J_{7exo\text{-}6} = J_{7exo\text{-}1}$ = 4 Hz, $J_{7exo\text{-}2}$ < 2 Hz, 1H, $H_{7exo}$), 1.60-1.40 (m, 2H, $H_{15}$), 1.45 (s, 15H, $C_5\underline{Me}_5$), 0.77 (m, ddd by decoupling, $J_{6\text{-}7endo}$ = 11.3 Hz, $J_{6\text{-}7exo} \approx J_{6\text{-}15} \approx$ 4 Hz, 1H, $H_6$). $^1H$-$^1H$ GCOSY (300 MHz, $CDCl_3$) δ 7.47 ($H_9$) ↔ δ 7.20 ($H_{11/10}$); δ 7.20[a] ($H_{11/10}$) ↔ δ 7.16 ($H_{12}$); δ 7.04 ($H_3$) ↔ δ 6.51 ($H_4$), δ 4.88 ($H_2$); δ 4.88 ($H_2$) ↔ δ 4.41 ($H_1$), δ 2.12 ($H_{7exo}$); δ 4.41 ($H_1$) ↔ δ 2.90 ($H_{7endo}$), δ 2.12 ($H_{7exo}$); δ 2.90 ($H_{7endo}$) ↔ δ 2.12 ($H_{7exo}$), δ 0.77 ($H_6$); δ 2.55 ($H_{14}$) ↔ δ 1.40 ($H_{15}$); δ 2.12 ($H_{7exo}$) ↔ δ 0.77 ($H_6$); δ 1.40 ($H_{15}$) ↔ δ 0.77[a] ($H_6$). [a]This correlation is most likely there, but insufficently resolved from the diagonal to be certain. $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 142.9 (s, $C_8$), 133.9 (s, $C_{13}$), 129.7 (d, $^1J_{CH}$ = 162 Hz, $C_{12}$), 128.5 (d, $^1J_{CH}$ = 161.8 Hz, $C_{11}$), 127.3 (d, $^1J_{CH}$ = 161.1 Hz, $C_{10}$), 124.5 (d, $^1J_{CH}$ = 161.1 Hz, $C_9$), 110.3 (s, $C_5$), 97.8 (s, $\underline{C}_5Me_5$), 97.7 (d, $^1J_{CH}$ = 165.6 Hz, $C_2$), 97.0[a] (d, $^1J_{CH} \approx$ 164 Hz, $C_3$), 90.5 (d, $^1J_{CH}$ = 157.0 Hz, $C_4$), 85.9 (d, $^1J_{CH}$ = 153.9 Hz, $C_1$), 47.9 (t, $^1J_{CH}$ = 135.8 Hz, $C_7$), 35.9 (d, $^1J_{CH}$ = 126.0 Hz, $C_6$), 27.8 (t, $^1J_{CH}$ = 129.3 Hz, $C_{15}$), 26.7 (t, $^1J_{CH} \approx$ 129 Hz, $C_{14}$), 8.8 (q, $^1J_{CH}$ = 129.1 Hz, $C_5\underline{Me}_5$). [a] This signal overlaps with the $C_5Me_5$ singlet in the gated spectrum. HMQC (300 MHz, $CDCl_3$) δ 129.7 ($C_{12}$) ↔ δ 7.16 ($H_{12}$); δ 128.5 ($C_{11}$) ↔ δ 7.20 ($H_{11/10}$); δ 127.3 ($C_{10}$) ↔ δ 7.20

($H_{11/10}$); δ 124.5 ($C_9$) ↔ δ 7.47 ($H_9$); δ 97.7 ($C_2$) ↔ δ 4.88 ($H_2$); δ 97.0 ($C_3$) ↔ δ 7.04 ($H_3$); δ 90.5 ($C_4$) ↔ δ 6.51 ($H_4$); δ 85.9 ($C_1$) ↔ δ 4.41 ($H_1$); δ 47.9 ($C_7$) ↔ δ 2.90 ($H_{7endo}$), δ 2.12 ($H_{7exo}$); δ 35.9 ($C_6$) ↔ δ 0.77 ($H_6$); δ 27.8 ($C_{15}$) ↔ δ 1.40 ($H_{15}$); δ 26.7 ($C_{14}$) ↔ δ 2.55 ($H_{14}$); δ 8.8 ($C_5\underline{Me_5}$) ↔ δ 1.45 ($C_5\underline{Me_5}$); HMBC (300 MHz, $CDCl_3$) δ 142.9 ($C_8$) ↔ δ 7.47 ($H_9$), δ 7.20 ($H_{11/10}$), δ 2.55 ($H_{14}$); δ 133.9 ($C_{13}$) ↔ δ 7.16 ($H_{12}$), δ 6.51 ($H_4$), δ 2.55 ($H_{14}$); δ 129.7 ($C_{12}$) ↔ δ 7.20 ($H_{11/10}$), δ 2.55 ($H_{14}$); δ 128.5 ($C_{11}$) ↔ δ 7.47 ($H_9$); δ 127.3 ($C_{10}$) ↔ δ 7.16 ($H_{12}$); δ 110.3 ($C_5$) ↔ δ 7.47 ($H_9$), δ 7.04 ($H_3$), δ 2.12 ($H_{7exo}$), δ 0.77 ($H_6$); δ 97.7[a] ($C_2$) ↔ δ 6.51 ($H_4$), δ 2.90 ($H_{7endo}$); δ 97.0 ($C_3$) ↔ δ 4.41 ($H_1$); δ 90.5 ($C_4$) ↔ δ 7.04 ($H_3$), δ 4.88 ($H_2$), δ 0.77 ($H_6$); δ 85.9 ($C_1$) ↔ δ 7.04 ($H_3$), δ 2.90 ($H_{7endo}$), δ 2.12 ($H_{7exo}$); δ 47.9 ($C_7$) ↔ δ 4.88 ($H_2$), δ 0.77 ($H_6$); δ 35.9 ($C_6$) ↔ δ 6.51 ($H_4$), δ 4.41 ($H_1$), δ 2.90 ($H_{7endo}$), δ 2.55 ($H_{14}$), δ 2.12 ($H_{7exo}$); δ 27.8 ($C_{15}$) ↔ δ 2.90 ($H_{7endo}$), δ 2.55 ($H_{14}$), δ 0.77 ($H_6$); δ 26.7 ($C_{14}$) ↔ δ 0.77 ($H_6$); δ 8.8 ($C_5\underline{Me_5}$) ↔ δ 1.45 ($C_5\underline{Me_5}$). [a]Signal overlaps with $\underline{C_5}Me_5$. The compound was recrystallized several times from dichloromethane/diethyl ether, but still did not give a satisfactory analysis. MS *m/z* calculated for $C_{25}H_{30}Co$ ($M^+$-H): 388.16013; found: 388.15994 (21 %).



**($\eta^5$-$C_5Me_5$)Co($\eta^4$-$C_7H_{10}$) (118).** To a Kontes flask was added ($C_5Me_5$)Co($C_2H_4$)$_2$ **(79)** (0.1140 g, 0.4555 mmol) and dried, degassed n-heptane (10 mL). 1-Vinylcyclopentene (122 μl, 2 equiv) was added, the Kontes valve was closed and the solution was heated to 65°C for 20 h. Solvent was removed from the resulting dark red solution *in vacuo* and the red residue was extracted with small amounts of pentane. The pentane solution was filtered through a Celite pad and dried. A dark red solid (0.1037 g, 79%) was obtained. $^1H$ NMR (400 MHz, $C_6D_6$) δ 4.44 (dd, $J$ = 8.2, 6.7 Hz, 1H, $H_2$), 2.45-2.35 (m, 2H,

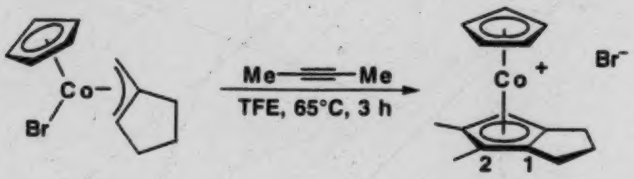
$CH_2$), 1.68 (s, 15H, $C_5Me_5$), 1.55-1.45 (m, 2H, $CH_2$), 1.40-1.25 (m, 2H, $CH_2$), 1.08 (d, *J* = 6.3 Hz, 1H, $H_{1exo}$), 0.63 (br s, 1H, $H_4$), -0.66 (d, *J* = 8.7 Hz, 1H, $H_{1endo}$); $^{13}C$ NMR (100 MHz, $C_6D_6$) δ 88.6, 73.5, 47.7, 37.7, 30.4, 29.3, 23.5, 10.1. MS *m/z* calculated for $C_{17}H_{25}Co$ ($M^+$): 288.12881; found: 288.12800 (12%).



**[($C_5Me_5$)Co($\eta^3$-$\eta^2$-$C_9H_{13}$)]$^+$ $BF_4^-$ (119) and [($C_5Me_5$)Co($\eta^5$-$C_{11}H_{15}$)]$^+$ $BF_4^-$ (120).** In the drybox, a Schlenk flask was charged with ($C_5Me_5$)Co($C_7H_{10}$) (**118**) (73.6 mg, 0.255 mmol) and removed to the Schlenk line. Dichloromethane (10 mL) was added and the solution was cooled to -78 °C. $HBF_4{\bullet}Et_2O$ (60 μL) was added and the solution was stirred for 1 min. Acetylene was then bubbled into the solution for 2 min and the solution was allowed to warm slowly to room temperature over a 12 h period. The solvent was reduced to about 3 mL and the product was precipitated by the addition of diethyl ether. The crude product was purified by redissolving in dichloromethane, filtering and precipitating with diethyl ether. An orange powder (91.0 mg, 89%) was obtained, consisting of a 10:1 mixture of complexes **119** and **120**. Data for major product **119**: IR ($CH_2Cl_2$ cast, $cm^{-1}$) 2962 (m), 1470 (m), 1455 (m), 1383 (m), 1281 (m), 1054 (s), 733 (w), 520 (m); $^1H$ NMR (400 MHz, $CDCl_3$) δ 4.18 (dd, $J_{2\text{-}1a}$ = 12.3 Hz, $J_{2\text{-}1s}$ = 8.0 Hz, 1H, $H_2$), 3.44 (dd, $J_{1s\text{-}2}$ = 8.0 Hz, $J_{1s\text{-}1a}$ = 2.5 Hz, 1H, $H_{1s}$), 3.18 (d, $J_{9s\text{-}8}$ = 7.9 Hz, 1H, $H_{9s}$), 2.75 (ddd, $J_{8\text{-}9a}$ = 13.7 Hz, $J_{8\text{-}9s}$ = 7.9 Hz, $J_{8\text{-}7}$ = 7.6 Hz, 1H, $H_8$), 2.64 (dd, *J* = 17.5, 6.1 Hz, 1H, $H_6$), 2.30-2.05 (m, 2H, $CH_2$), 2.0-1.6$^a$ (series of m, 3H, $CH_2$, $H_{9a}$), 1.73 (s, 15H, $C_5\underline{Me_5}$), 0.98 (dd, $J_{1a\text{-}2}$ = 12.2 Hz, $J_{1a\text{-}1s}$ = 2.5 Hz, 1H, $H_{1a}$), 0.91 (dd $J_{7\text{-}8}$ = 7.6 Hz, $J_{7\text{-}6}$ = 7.2 Hz, 1H, $H_7$). $^a$The $H_{9a}$ proton is located at about δ 1.95 by decoupling experiments. $^1H$-$^1H$ GCOSY (300 MHz, $CDCl_3$) δ

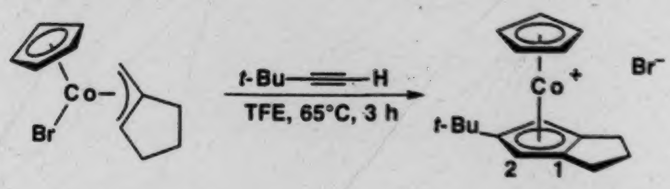
4.18 ($H_2$) ↔ δ 3.44 ($H_{1s}$), δ 0.98 ($H_{1a}$); δ 3.44 ($H_{1s}$) ↔ δ 0.98 ($H_{1a}$); δ 3.18 ($H_{9s}$) ↔ δ 2.75 ($H_8$), δ 1.95 ($H_{9a}$); δ 2.75 ($H_8$) ↔ δ 1.95 ($H_{9a}$), δ 0.91 ($H_7$); δ 2.64 ($H_6$) ↔ δ 2.17 ($CH_2$), δ 1.80 ($CH_2$), δ 0.91 ($H_7$); δ 2.17 ($CH_2$) ↔ δ 1.80 ($CH_2$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 97.9 (s, $\underline{C}_5Me_5$), 86.0 (d, $^1J_{CH}$ = 162.7 Hz, $C_2$), 81.1 (s, $C_3$), 62.9 (t, $^1J_{CH}$ = 160.4 Hz, $C_9$), 54.2 (t, $^1J_{CH}$ = 161.6 Hz, $C_1$), 42.3 (d, $^1J_{CH}$ = 166.3 Hz, $C_8$), 37.0 (d, $^1J_{CH}$ = 144.0 Hz, $C_7$), 32.4 (t, $^1J_{CH}$ = 132.7 Hz, $C_6$), 30.8 (t, $^1J_{CH}$ = 135.3 Hz, $C_{4/5}$), 24.3 (t, $^1J_{CH}$ = 131.9 Hz, $C_{4/5}$), 9.3 (q, $^1J_{CH}$ = 129.0 Hz, $C_5\underline{Me}_5$); HMQC (300 MHz, $CDCl_3$) δ 86.0 ($C_2$) ↔ δ 4.18 ($H_2$); δ 62.9 ($C_9$) ↔ δ 3.18 ($H_{9s}$), δ 1.95 ($H_{9a}$); δ 54.2 ($C_1$) ↔ δ 3.44 ($H_{1s}$), δ 0.98 ($H_{1a}$); δ 42.3 ($C_8$) ↔ δ 2.75 ($H_8$); δ 37.0 ($C_7$) ↔ δ 0.91 ($H_7$); δ 32.4 ($C_6$) ↔ δ 2.64 ($H_6$), δ 2.1 ($H_6$); δ 30.8 ($CH_2$) ↔ δ 2.0 ($CH_2$), δ 1.8 ($CH_2$); δ 24.3 ($CH_2$) ↔ δ 2.2 ($CH_2$), δ 1.9 ($CH_2$); δ 9.3 ($C_5\underline{Me}_5$) ↔ δ 1.73 ($C_5\underline{Me}_5$); HMBC (300 MHz, $CDCl_3$) δ 97.9 ($\underline{C}_5Me_5$) ↔ δ 1.73 ($C_5\underline{Me}_5$); δ 86.0 ($C_2$) ↔ δ 3.44 ($H_{1s}$), δ 0.91 ($H_7$); δ 81.1 ($C_3$) ↔ δ 4.18 ($H_2$), δ 3.44 ($H_{1s}$), δ 2.64 ($H_6$), δ 0.98 ($H_{1s}$); δ 62.9 ($C_9$) ↔ δ 2.75 ($H_8$), δ 0.91 ($H_7$); δ 42.3 ($C_8$) ↔ δ 3.18 ($H_{9s}$), δ 0.91 ($H_7$); δ 37.0 ($C_7$) ↔ δ 4.18 ($H_2$), δ 3.18 ($H_{9s}$), δ 2.75 ($H_8$), δ 1.95 ($H_{9s}$); δ 30.8 ($C_{4/5}$) ↔ δ 2.64 ($H_6$); δ 24.3 ($C_{4/5}$) ↔ δ 0.91 ($H_7$). Even after recrystallization from dichloromethane/diethyl ether, the sample was not analytically pure. Analysis calculated for $C_{19}H_{28}BCoF_4$: C, 56.74; H, 7.02; found: C, 52.914; H, 6.976. Electrospray MS *m/z* . No parent ion could be seen.

Data for minor complex (**120**). Note that chemical shift and coupling constant values are approximate as signals are sometimes obscured by the major compound or otherwise poorly resolved. $^1H$ NMR (400 MHz, $CDCl_3$) δ 6.65 (t, $J$ = 7 Hz, 1H), 5.22 (t, $J$ = 7 Hz, 1H), 4.90 (t, $J$ = 8 Hz, 1H), 4.3-4.2 (m, 2H), 1.87 (s, 15H, $C_5Me_5$), 0.82 (dd, $J$ = 13, 4 Hz, 1H). A further signal (δ 1.95) is obscured in the Cp* region, but is located in the COSY spectrum. $^1H$-$^1H$ GCOSY (300 MHz, $CDCl_3$) δ 6.65 ↔ δ 5.22, δ 4.90; δ 5.22 ↔ δ 4.25; δ 4.90 ↔ δ 4.25; δ 4.25 ↔ δ 1.95, δ 0.82; δ 1.95 ↔ δ 0.82.



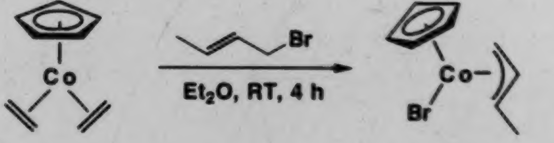
110 121

**[(2,3-dimethylbicyclo[3.3.0]2,4-octadien-1-yl)Co($C_5H_5$)]$^+$ Br$^-$ (121).** To a flask equipped with a Kontes valve was added ($C_5H_5$)Co($\eta^3$-$C_6H_9$)Br (**110**) (47.8 mg, 0.168 mmol) in the drybox. The flask was removed to the Schlenk line, where 2,2,2-trifluoroethanol (8 mL) was used to dissolve the solid. 2-butyne (0.26 mL, 20 equiv) was then added and the Kontes valve was sealed. The entire flask was then immersed in an oil bath and heated to 65°C for 3 h, at which time the color of the solution had lightened considerably. All volatiles were removed *in vacuo* and the residue purified by elution through a pipet filled with silica gel. After a brown band, a light yellow band was collected using 5% methanol/dichloromethane as the eluent. The oily yellow solid was purified by two recrystallizations from dichloromethane/diethyl ether to yield a yellow powder (12.6 mg, 22%). IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3027 (s), 2949 (s), 2909 (m), 1652 (w), 1486 (w), 1466 (s), 1455 (s), 1429 (m), 1415 (s), 1378 (s), 1336 (w), 1300 (w), 1270 (m), 1110 (m), 1036 (s), 1009 (m), 980 (w), 889 (m), 858 (s), 799 (w), 740 (m), 653 (w), 498 (w), 450 (s), 431 (s); $^1$H NMR (360 MHz, $CDCl_3$) δ 5.62 (s, 1H, $H_4$), 5.46 (s, 5H, $C_5\underline{H}_5$), 2.71 (dd, $J = 16.4, 7.2$ Hz, 1H, $CH_2$), 2.62 (dd, $J = 16.4, 6.9$ Hz, 1H, $CH_2$), 2.55-2.40 (m, 2H, $CH_2$), 2.30-2.15 (m, 2H, $CH_2$), 2.12 (s, 3H, Me), 2.09 (s, 3H, Me); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 111.3 ($C_{quat}$), 109.0 ($C_{quat}$), 103.6 ($C_{quat}$), 93.4 ($C_{quat}$), 85.9 ($\underline{C}_5H_5$), 75.4 (CH), 29.2 ($CH_2$), 26.6 ($CH_2$), 25.0 ($CH_2$), 14.3 ($CH_3$), 12.4 ($CH_3$). Electrospray MS *m/z* calculated for $C_{15}H_{18}Co$ ($M^+$ -Br): 257.074049; found: 257.074379 (100%). Analysis calculated for $C_{15}H_{18}BrCo$: C, 53.44; H, 5.38; found: C, 52.982; H, 4.976.



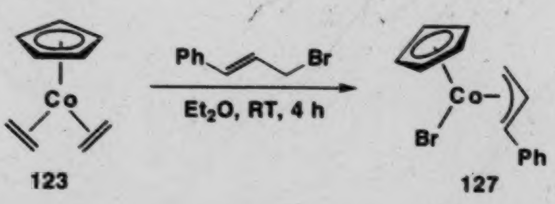
**110** **122**

**[(η$^5$-3-*t*-butylbicyclo[3.3.0]2,4-octadien-1-yl)Co($C_5H_5$)]$^+$ Br$^-$ (122).** To a flask equipped with a Kontes valve was added ($C_5H_5$)Co(η$^3$-$C_6H_9$)Br (**110**) (49.6 mg, 0.174 mmol) in the drybox. The flask was removed to the Schlenk line, where 2,2,2-trifluoroethanol (8 mL) was used to dissolve the solid. 3,3-Dimethyl-1-propyne (0.43 mL, 20 equiv) was then added and the Kontes valve was sealed. The entire flask was then immersed in an oil bath and heated to 65°C for 3 h, at which time the color of the solution had lightened considerably. All volatiles were removed *in vacuo* and the residue purified by elution through a pipet filled with silica gel. After an orange band, a light yellow band was collected using 5% methanol/dichloromethane as the eluent. The yellow solid was purified by recrystallization from dichloromethane/diethyl ether to yield a yellow powder (32.2 mg, 51%). IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3045 (s), 2961 (s), 2906 (m), 1652 (m), 1616 (w), 1482 (s), 1464 (s), 1436 (m), 1416 (s), 1386 (m), 1370 (s), 1268 (w), 1228 (m), 1037 (s), 860 (m), 733 (w), 687 (w), 514 (m), 464 (m), 431 (s), 410 (s); $^1$H NMR (360 MHz, $CDCl_3$) δ 5.63 (s, 5H, $C_5\underline{H}_5$), 5.49 (s, 2H, $H_{2,4}$), 2.77 (dd, *J* = 16.6, 6.7 Hz, 2H, $CH_2$), 2.50-2.40 (m, 2H, $CH_2$), 2.30-2.15 (m, 2H, $CH_2$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 122.8 ($C_{quat}$), 112.5 ($C_{quat}$), 85.1 ($\underline{C}_5H_5$), 72.6 (CH), 31.3 ($C_{quat}$), 31.0 (*t*-butyl), 29.2 ($CH_2$), 25.7 ($CH_2$). Electrospray MS *m/z* calculated for $C_{17}H_{22}Co$ ($M^+$-Br): 285.105349; found: 285.105250 (100%).



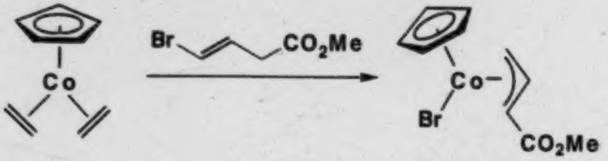
**123** **126**

**$(C_5H_5)Co(1\text{-}Me\text{-}C_3H_4)Br$ (126).** $(C_5H_5)Co(C_2H_4)_2$ **(123)** (327.6 mg, 1.819 mmol) was dissolved in diethyl ether (20 mL) under a nitrogen atmosphere. 1-bromo-2-butene (210 μl, 2.04 mmol, 1.13 equiv) was added via syringe at room temperature. The solution was stirred for 4 h, then the solvent was removed *in vacuo*. The residue was extracted with toluene and the solution was filtered through a Celite pad. Removal of the solvent gave a dark red-black solid (336.7 mg, 71%). $^1H$ NMR (400 MHz, $C_6D_6$) δ 4.52 (d, *J* = 7.4 Hz, 1H, $H_{3a}$), 4.35 (s, 5H, $C_5\underline{H}_5$), 3.8-3.9 (m, 1H, $H_1$), 3.70 (td, *J* = 12.3, 7.6 Hz, 1H, $H_2$), 2.81 (d, *J* = 12.3 Hz, 1H, $H_{3s}$), 1.36 (d, *J* = 6.4 Hz, 3H, $CH_3$); $^1H$ NMR (360 MHz, $CD_2Cl_2$) δ 5.04 (d, *J* = 7.5 Hz, 1H, $H_{3a}$), 4.99 (s, 5H, $C_5\underline{H}_5$), 4.48 (td, *J* = 12.2, 7.5 Hz, 1H, $H_2$), 3.60 (br dq, *J* = 12, 6 Hz, 1H, $H_1$), 2.49 (d, *J* = 12.6 Hz, 1H, $H_{3s}$), 1.87 (d, *J* = 6.5 Hz, 3H, $CH_3$); $^{13}C$ NMR (75 MHz, $C_6D_6$) δ 89.3 ($C_2$), 84.3 ($\underline{C}_5H_5$), 77.9 ($C_1$), 50.7 ($C_3$), 22.2 ($CH_3$). Analysis calculated for $C_9H_{12}BrCo$: C, 41.73; H, 4.67; found: C, 41.555; H, 4.367.

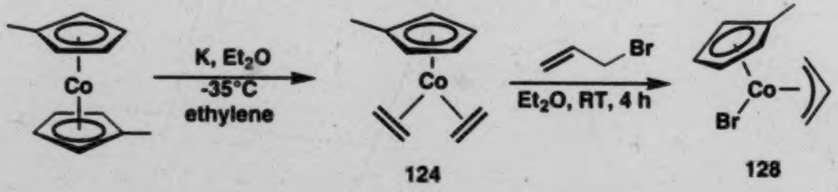


**$(C_5H_5)Co(1\text{-}Ph\text{-}C_3H_4)Br$ (127).** $(C_5H_5)Co(C_2H_4)_2$ **(123)** (292.9 mg, 1.626 mmol) was dissolved in diethyl ether (15 mL) under a nitrogen atmosphere. Cinnamyl bromide (270 μl, 1.82 mmol, 1.12 equiv) was added via syringe at room temperature. The solution was stirred for 4 h before all volatile material was removed *in vacuo*. The residue was then extracted with toluene and the solution was filtered through a Celite pad. Removal of the solvent was followed by recrystallization of the residue from toluene-pentane at -35 °C to give a black solid (341 mg, 65%). $^1H$ NMR (300 MHz, $CD_2Cl_2$) δ 7.68 (d, *J* = 7.2 Hz, 2H, $H_4$), 7.44 (t, *J* = 7.0 Hz, 1H, $H_6$), 7.35 (t, *J* = 6.9 Hz, 2H, $H_5$), 5.39 (td, *J* = 12.4, 7.9 Hz, 1H, $H_2$), 5.28 (d, *J* = 7.7 Hz, 1H, $H_{3a}$), 4.81 (s, 5H, $C_5\underline{H}_5$), 4.47 (d, *J* = 12.6 Hz, 1H, $H_{1s}$), 2.88 (d, *J* = 12.4 Hz, 1H, $H_{3s}$); $^{13}C$ NMR (75 MHz, $CD_2Cl_2$) δ 142.5 ($C_4$), 129.9 ($C_{5,6}$), 127.6

($C_7$), 126.2 ($C_{5/6}$), 86.0 ($\underline{C}_5H_5$), 84.6 ($C_2$), 79.7 ($C_1$), 51.8 ($C_3$). Analysis calculated for $C_{14}H_{14}BrCo$: C, 52.37; H, 4.40; found: C, 52.273; H, 4.377.

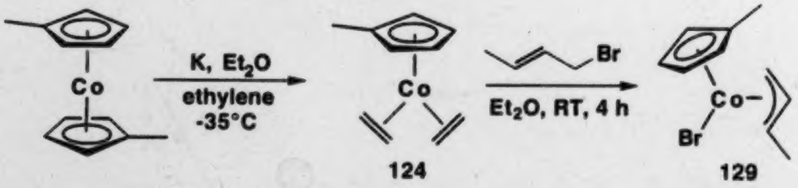


**($C_5H_5$)Co(1-($CO_2Me$)-$\eta^3$-$C_3H_4$)(Br).** A Schlenk flask was charged in the drybox with ($C_5H_5$)Co($C_2H_4$)$_2$ (**123**) (0.1877 g, 1.042 mmol) and removed to the Schlenk line, where dry, degassed tetrahydrofuran (10 mL) was added, followed immediately by methyl 4-bromocrotonate (0.205 g, 1.1 equiv). The light orange solution turned dark purple-red and was stirred overnight to allow the reaction to go to completion. All volatile material was removed *in vacuo* and the residue was extracted with dry toluene. The toluene extract was filtered through a Celite pad and the solvent was removed. The residue was recrystallized from toluene/pentane to give a dark purple solid (0.203 g, 64%). $^1H$ NMR (300 MHz, $CD_2Cl_2$) δ 5.56 (ddd, $J$ = 13.4, 11.5, 8.1 Hz, 1H, $H_c$), 5.30 (d, $J$ = 8.1 Hz, 1H, $H_{3s}$), 5.15 (s, 5H, $C_5\underline{H}_5$), 3.88 (s, 3H, $CO_2\underline{Me}$), 3.16 (d, $J$ = 11.4 Hz, 1H, $H_{1a}$), 2.94 (d, $J$ = 13.5 Hz, 1H, $H_{3a}$); $^{13}C$ NMR (75 MHz, $CD_2Cl_2$) δ 92.4, 86.4 ($\underline{C}_5H_5$), 60.3, 57.7, 52.5. The carbonyl carbon was not located above baseline noise. Analysis calculated for $C_{10}H_{12}BrCoO_2$: C, 39.63; H, 3.99; found: C, 39.425; H, 3.912.



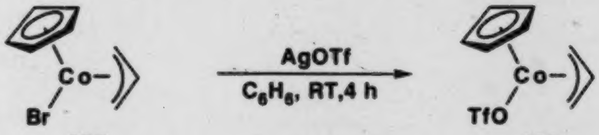
**($C_5H_4Me$)Co($\eta^3$-$C_3H_5$)(Br) (128).** In the drybox, 1,1'-dimethylcobaltocene (3.91 g, 18.0 mmol) was weighed into a Schlenk flask and dissolved in diethyl ether (100 mL). The flask was capped with a solid addition tube containing potassium sand (1.01 g, 1.4 equiv). The apparatus was taken outside the glove box and cooled to -35 °C under an ethylene atmosphere. The potassium was then added and the slurry was stirred under ethylene for 16 h. The resulting orange suspension was cooled to -50 °C and the Cp'K allowed to settle. The mixture was filtered through Celite at -50 °C, under $N_2$ and the dark red filtrate was divided into 2 equal aliquots.

To one aliquot, diethyl ether was added to a total volume of 50 mL. To this solution, allyl bromide (0.76 mL, 9 mmol, 1.0 equiv) was added. The solution was stirred for 4 h at room temperature. All volatile material was then removed *in vacuo* and the residue was extracted with dry toluene. The toluene extracts were filtered through Celite and concentrated until crystals began to form. The solution was then diluted with an equal volume of pentane and cooled to -60 °C. The resulting dark red-black crystals (280 mg, 12%) were collected by vacuum filtration. $^1$H NMR (400 MHz, $CDCl_3$) δ 4.70 (d, *J* = 7.6 Hz, 2H, $H_s$), 4.62-4.60 (m, 2H, $C_5\underline{H}_4Me$), 4.42-4.40 (m, 2H, $C_5\underline{H}_4Me$), 4.09 (tt, *J* = 13.0, 7.7 Hz, 1H, $H_c$), 2.76 (d, *J* = 13.0 Hz, 2H, $H_a$), 1.64 (s, 3H, $C_5H_4\underline{Me}$); $^1$H NMR (400 MHz, $C_6D_6$) δ 4.47 (d, 7.5 Hz, 2H, $H_s$), 4.4-4.3 (m, 2H, $C_5\underline{H}_4Me$), 3.9-3.8 (m, 2H, $C_5\underline{H}_4Me$), 3.76 (tt, *J* = 13.0, 7.6 Hz, 1H, $H_c$), 3.08 (d, *J* = 12.9 Hz, 2H, $H_a$), 1.56 (s, 3H, $C_5H_4\underline{Me}$); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 89.6 ($C_c$), 85.8 ($\underline{C}_5H_4Me$), 80.1 ($\underline{C}_5H_4Me$), 55.6 ($C_t$), 13.6 ($C_5H_4\underline{Me}$). The quaternary carbon was not found. Analysis calculated for $C_9H_{12}BrCo$: C, 41.73; H, 4.67; found: C, 41.826; H, 4.706.



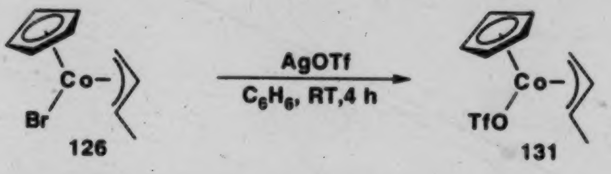
**($C_5H_4Me$)Co($\eta^3$-1-Me-$C_3H_4$)(Br) (129).** In the drybox, 1,1'-dimethylcobaltocene (3.91 g, 18.0 mmol) was weighed into a Schlenk flask, and dissolved in diethyl ether (100 mL). The flask was capped with a solid addition tube containing potassium sand (1.01 g, 1.4 equiv). The apparatus was taken outside the glove box and cooled to -35 °C under an ethylene atmosphere. The potassium was then added and the slurry was stirred under ethylene for 16 h. The resulting orange suspension was cooled to -50 °C and the Cp'K allowed to settle. The mixture was filtered through Celite at -50 °C, under $N_2$ and the dark red filtrate was divided into 2 equal aliquots.

To one aliquot, diethyl ether was added to a total volume of 50 mL. To this solution, crotyl bromide (0.91 mL, 9 mmol, 1.0 equiv) was added. The solution was stirred for 4 h at room temperature. All volatiles were then removed *in vacuo* and the residue was extracted with dry toluene. The toluene extracts were filtered through Celite and concentrated until crystals began to form. The solution was then diluted with an equal volume of pentane and cooled to -60 °C. The resulting dark red-black crystals (250 mg, 10%) were collected. $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 4.54 (br s, 1H, $C_5\underline{H}_4Me$), 4.34 (d, $J$ = 7.5 Hz, 1H, $H_s$), 4.19 (br s, 1H, $C_5\underline{H}_4Me$), 3.84 (dt, $J$ = 12.2, 6.6 Hz, 1H, $H_c$), 3.75-3.6 (m, 3H, $H_a$, $C_5\underline{H}_4Me$, $H_{1a}$), 2.90 (d, $J$ = 12.6 Hz, 1H, $H_{3a}$), 1.66 (s, 3H, $C_5H_4\underline{Me}$), 1.34 (d, $J$ = 6.6 Hz, 3H, $C_3H_4\underline{Me}$); $^{13}C$ NMR (100 MHz, $C_6D_6$) $\delta$ 90.5 ($C_2$), 88.7 ($\underline{C}_5H_4Me$), 85.6 ($\underline{C}_5H_4Me$), 81.3 ($\underline{C}_5H_4Me$), 78.3 ($C_1$), 76.4 ($\underline{C}_5H_4Me$), 50.5 ($C_3$), 22.1 ($C_3H_4\underline{Me}$), 13.7 ($C_5H_4\underline{Me}$). The quaternary carbon of the methylcyclopentadienyl ring was not observed. Analysis calculated for $C_{10}H_{14}BrCo$: C, 43.99; H, 5.17; found: C, 44.155; H, 5.003.

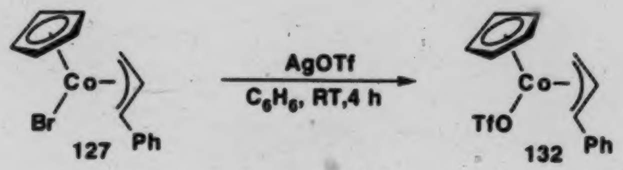


125 130

**$(C_5H_5)Co(\eta^3\text{-}C_3H_5)(OTf)$ (130).** $(C_5H_5)Co(\eta^3\text{-}C_3H_5)Br$ (**125**) (95.3 mg, 0.389 mmol) was dissolved in benzene (15 mL) in the drybox. Silver triflate (0.1177 g, 0.4581 mmol, 1.18 equiv) was added. After stirring 4 h, the solution was filtered through a Celite pad. The solution was reduced to dryness and the residue was extracted with benzene (6 mL). Filtration through Celite was followed by removal of the solvent to give a brown solid (99.3 mg, 81%). The analytical sample was crystallized from toluene/pentane at -35 °C, although analytical purity was still not obtained. IR ($C_6H_6$ cast, cm$^{-1}$) 1256 (s), 1168 (s), 1030 (m), 637 (m), 516 (w); $^1$H NMR (300 MHz, $C_6D_6$) δ 5.06 (d, *J* = 7.7 Hz, 2H, $H_a$), 4.32 (s, 5H, $C_5\underline{H}_5$), 3.67 (tt, *J* = 13.5, 7.6 Hz, 1H, $H_c$), 2.27 (d, *J* = 13.4 Hz, 2H, $H_s$); $^{13}$C NMR (75 MHz, $C_6D_6$) δ 94.8 ($C_2$), 83.6 ($\underline{C}_5H_5$), 62.9 ($C_1$); MS *m/z* calculated for $C_9H_{10}CoF_3O_3S$ ($M^+$): 313.96347; found: 313.96325 (28%); *m/z* calculated for $C_8H_{10}Co$ ($M^+$- $CF_3SO_3^-$): 165.01144; found: 165.01116 (100%). Analysis calculated for $C_9H_{10}CoF_3SO_3$: C, 34.41; H, 3.21; S, 10.20; found: C, 30.528; H, 2.896; S, 10.519.

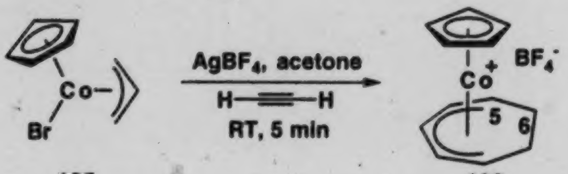


**($C_5H_5$)Co(1-Me-$\eta^3$-$C_3H_4$)(OTf) (131).** ($C_5H_5$)Co(1-Me-$\eta^3$-$C_3H_4$)Br (**126**) (104.5 mg, 0.4035 mmol) was dissolved in benzene (12 mL) in the drybox. Silver triflate (121.7 mg, 0.4737 mmol, 1.17 equiv) was added. After stirring 4 h, the solution was filtered through a Celite pad. Removal of the solvent gave a brown powder (98.9 mg, 75%). The analytical sample was crystallized from toluene/pentane at -35 °C, although analytical purity was still not obtained. IR ($C_6H_6$ cast, cm$^{-1}$) 1437 (w), 1407 (w), 1379 (w), 1289 (s), 1246 (s), 1169 (s), 1030 (s), 638 (m); $^1$H NMR (300 MHz, $C_6D_6$) δ 5.07 (d, *J* = 7.7 Hz, 1H, $H_{3a}$), 4.39 (s, 5H, $C_5\underline{H}_5$), 3.76 (td, *J* = 12.7, 7.8 Hz, 1H, $H_2$), 3.04 (dq, *J* = 13.1, 6.7 Hz, 1H, $H_1$), 2.15 (d, *J* = 13.0 Hz, 1H, $H_{3s}$), 1.45 (d, *J* = 6.5 Hz, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $C_6D_6$) δ 94.9 ($C_2$), 85.7 ($C_1$), 84.1 ($\underline{C}_5H_5$), 57.2 ($C_3$), 21.9 ($CH_3$). Analysis calculated for $C_{10}H_{12}CoF_3O_3S$: C, 36.60; H, 3.69; S, 9.77; found: C, 36.069; H, 3.858; S, 9.500.



**$(C_5H_5)Co(1\text{-}Ph\text{-}\eta^3\text{-}C_3H_4)(OTf)$ (132).** In the drybox, $(C_5H_5)Co(1\text{-}Ph\text{-}\eta^3\text{-}C_3H_4)Br$ (**127**) (100.2 mg, 0.3120 mmol) was dissolved in benzene (12 mL). Silver triflate (98.3 mg, 0.383 mmol, 1.23 equiv) was added. After stirring 4 h, the solution was filtered through a Celite pad. Removal of the solvent gave a brown powder (65.1 mg, 53%). IR ($CH_2Cl_2$ cast, $cm^{-1}$) 1289 (s), 1239 (s), 1226 (s), 1168 (m), 1029 (s), 638 (m); $^1H$ NMR (300 MHz, $C_6D_6$) $\delta$ 7.60 (d, *J* = 7.4 Hz, 2H, $H_4$), $\delta$ 7.29 (apparent t, *J* = 7.4, 7.2 Hz, 1H, $H_6$), 7.60 (apparent t, *J* = 7.4, 7.2 Hz, 2H, $H_5$), 5.45 (d, *J* = 7.7 Hz, 1H, $H_{3a}$), 4.97 (td, *J* = 12.9, 7.7 Hz, 1H, $H_2$), 4.38 (s, 5H, $C_5\underline{H}_5$), 4.04 (d, *J* = 13.0 Hz, 1H, $H_1$), 2.39 (d, *J* = 12.9 Hz, 1H, $C_{3s}$); $^{13}C$ NMR (75 MHz, $C_6D_6$) $\delta$ 141.5 ($C_{Ph,ipso}$), 129.9 ($C_{4/5}$), 128.2 ($C_6$), 126.8 ($C_{4/5}$), 89.2 ($C_2$), 85.4 ($C_1$), 84.9 ($\underline{C}_5H_5$), 58.5 ($C_3$). Analysis calculated for $C_{15}H_{14}CoF_3O_3S$: C, 46.17; H; 3.62; found: C, 46.124; H; 3.451.

**General Note.** The Cp cycloheptadienyl complexes proved more difficult to purify, due in part to a lower yield and also to difficulty encountered in recrystallization. Unlike the Cp* analogues, the separation of the impurities is incomplete. The complexes give rise to clean NMR spectra; however, accurate combustion analyses could not be obtained; the best results are nonetheless reported.

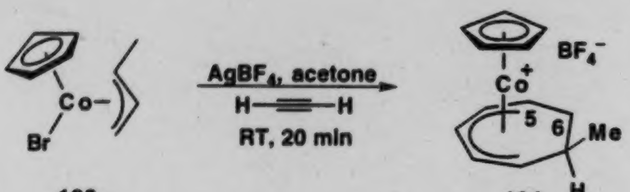


125

133

**$[(C_5H_5)Co(\eta^5\text{-}C_7H_9)]^+ BF_4^-$ (133).** To a Schlenk flask was added $(C_5H_5)Co(C_3H_5)(Br)$ (**125**) (0.1307 g, 0.5334 mmol) and reagent grade acetone (15 mL). Silver tetrafluoroborate (0.1152 g, 0.5917 mmol, 1.1 equiv) was added, and the solution was stirred briefly. Acetylene was then bubbled into the resulting suspension for 5 min. The reaction mixure was filtered and the solvent was removed *in vacuo*. The crude product was then purified using flash chromatography (silica gel, 7% methanol/dichloromethane).

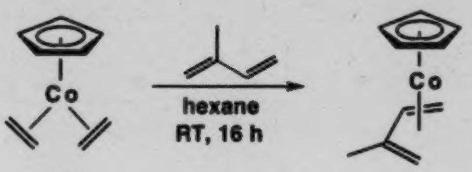
A light orange powder (52.6 mg, 47%) was obtained. IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3118(m), 3078 (m), 3049 (w), 2956 (m), 2879 (m), 2837 (w), 1445 (w), 1430 (m), 1409 (m), 1365 (m), 1309 (w), 1070 (s), 1045 (s), 1037 (s), 1012 (m), 979 (m), 952 (w), 883 (w), 859 (m), 833 (m), 818 (w), 734 (m), 521 (m), 507 (m), 479 (m); $^1H$ NMR (300 MHz, acetone-$d_6$) δ 7.41 (t, $J$ = 6.6 Hz, 1H, $H_3$), 5.80 (t, $J \approx 6$ Hz, 2H, $H_{2/4}$, overlap with Cp), 5.78 (s, 5H, $C_5\underline{H}_5$), 5.60 (br s, 2H, $H_{1/5}$), 2.49 (m, 2H, $H_{6endo/7endo}$), 1.25 (m, 2H, $H_{6exo/7exo}$); $^1H$-$^1H$ COSY (400 MHz, $CD_2Cl_2$) δ 7.41 ($H_3$) ↔ δ 5.80 ($H_{2/4}$); δ 5.80 ↔ δ 5.60 ($H_{1/5}$), δ 2.49 (w, $H_{6endo/7endo}$), δ 1.25 (w, $H_{6exo/7exo}$); δ 5.60 ($H_{1/5}$) ↔ δ 2.49 ($H_{6endo/7endo}$); δ 1.25 ($H_{6exo/7exo}$); δ 2.49 ($H_{6endo/7endo}$) ↔ δ 1.25 ($H_{6exo/7exo}$); $^{13}C$ NMR (100 MHz, $CD_2Cl_2$) δ 101.4 (dt, $^1J_{CH}$ = 172.6 Hz, $^2J_{CH}$ = 9.1 Hz, $C_3$), 95.2 (d, $^1J_{CH}$ = 171.1 Hz, $C_{2/4}$), 89.4 (dd, $^1J_{CH}$ = 160.0 Hz, $^2J_{CH}$ = 6.3 Hz, $C_{1/5}$), 87.3 (d(quintet), $^1J_{CH}$ = 183.1 Hz, $^2J_{CH}$ = 6.1 Hz, $\underline{C}_5H_5$), 34.6 (t, $^1J_{CH}$ = 135.5 Hz, $C_{6/7}$). Analysis calculated for $C_{12}H_{14}CoBF_4$: C, 47.41; H, 4.64; found: C, 47.255; H, 4.471.



126

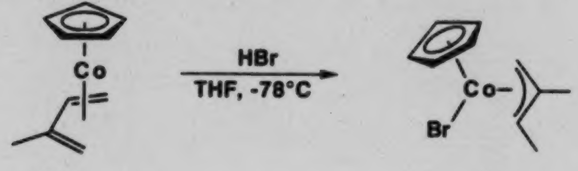
134

**[($C_5H_5$)Co($\eta^5$-1-Me-$C_7H_8$)]$^+$ $BF_4^-$ (134).** To a Schlenk flask was added ($C_5H_5$)Co($\eta^3$-1-Me-$C_3H_4$)(Br) **(126)** (0.7815 g, 3.017 mmol) and reagent grade acetone (approximately 100 mL). Silver tetrafluoroborate (0.617 g, 3.17 mmol, 1.05 equiv) was added, and the solution was stirred for 20 min. The resulting suspension was filtered to remove silver salts and the filtrate was cooled to 0°C. Acetylene was then bubbled into the solution for 20 min. The reaction mixure was warmed slowly over 5 h to room temperature. The solvent was removed *in vacuo* and the crude product was then filtered through a short (2 cm) silica pad using 10% methanol/dichloromethane. A dark red solution was obtained which gave a dark red powder (0.6657g, 69%) upon drying. The analytical sample was recrystallized from dichloromethane/diethyl ether, although analytical purity was still not obtained. IR ($CH_2Cl_2$ cast $cm^{-1}$) 3118 (m), 2966 (m), 2934 (m), 2877 (m), 1460 (m), 1431 (m), 1411 (m), 1375 (m), 1361 (w), 1298 (m), 1285 (m), 1053 (s), 1037 (s), 967 (m), 916 (w), 858 (m), 833 (m), 734 (w), 701 (w), 521 (m), 501 (m), 477 (m); $^1H$ NMR (300 MHz, acetone-$d_6$) $\delta$ 7.41 (t, $J$ = 6.6 Hz, 1H, $H_3$), 5.80 (t, overlap with Cp, $J \approx 8$ Hz, 1H, $H_4$), 5.78 (s, 5H, $C_5\underline{H}_5$), 5.75 (t, $J \approx 7$ Hz, 1H, $H_2$), 5.49 (dddd, $J$ = 8.5, 6.3, 4.0, 0.8 Hz, 1H, $H_5$), 5.31 (dd, $J$ = 8.7, 3.5 Hz, 1H, $H_1$), 2.09 (dtd, $J$ = 14.9, 5.5, 0.8 Hz, 1H, $H_{6endo}$), 1.57 (m, 1H, $H_{7exo}$), 1.36 (d, $J$ = 6.7 Hz, 3H, $CH_3$), 1.30 (dtd, $J$ = 15.0, 4.2, 1.3 Hz, 1H, $H_{6exo}$); $^1H$-$^1H$ COSY (400 MHz, $CD_2Cl_2$) $\delta$ 7.41 ($H_3$) $\leftrightarrow$ $\delta$ 5.80 ($H_4$), $\delta$ 5.75 ($H_2$), $\delta$ 5.31 (w, $H_1$), $\delta$ 5.49 (w, $H_5$); $\delta$ 5.80 ($H_4$) $\leftrightarrow$ $\delta$ 5.49 ($H_5$); $\delta$ 5.75 ($H_2$) $\leftrightarrow$ $\delta$ 5.31 ($H_1$), $\delta$ 1.57 ($H_{7exo}$), $\delta$ 1.30 ($H_{6exo}$); $\delta$ 5.49 ($H_5$) $\leftrightarrow$ $\delta$ 2.09 ($H_{6endo}$), $\delta$ 1.36 (Me), $\delta$ 1.30 ($H_{6exo}$); $\delta$ 2.09 ($H_{6exo}$) $\leftrightarrow$ $\delta$ 1.57 ($H_{7exo}$), $\delta$ 1.30 ($H_{6exo}$); $\delta$ 1.57 ($H_{7exo}$) $\leftrightarrow$ $\delta$ 1.36 (Me), $\delta$ 1.30 (w, $H_{6exo}$); $^{13}C$ NMR (100 MHz, $CD_2Cl_2$) $\delta$ 101.2 (dt, $^1J_{CH}$ = 173.4 Hz, $^2J_{CH}$ = 9.6 Hz, $C_3$), 95.4 (d, $^1J_{CH}$ = 170.4 Hz, $C_4$), 95.0 (d, $^1J_{CH}$ = 154.0 Hz, $C_1$), 93.6 (d, $^1J_{CH}$ = 152.8 Hz, $C_2$), 87.1 (dp, $^1J_{CH}$ = 183.7 Hz, $^2J_{CH}$ = 6.6 Hz, $\underline{C}_5H_5$), 87.1 (d, $^1J_{CH} \approx 180$ Hz, $C_5$)(overlaps with Cp), 41.5 (t, $^1J_{CH}$ = 128 Hz, $C_6$), 41.2 (d, $^1J_{CH}$ = 126.8 Hz, $C_7$), 22.8 (q, $^1J_{CH}$ = 125.5 Hz, Me); $^1H$-$^{13}C$ HETCORR (100 MHz, $CD_2Cl_2$) $\delta$ 101.2 ($C_3$) $\leftrightarrow$ $\delta$ 7.41 ($H_3$); $\delta$ 95.4 ($C_4$) $\leftrightarrow$ $\delta$ 5.80 ($H_4$); $\delta$ 95.0 ($C_1$) $\leftrightarrow$ $\delta$ 5.31 ($H_1$); $\delta$ 93.6 ($C_2$) $\leftrightarrow$ $\delta$ 5.75 ($H_2$); $\delta$ 87.1 ($C_5$) $\leftrightarrow$ $\delta$ 5.49 ($H_5$); $\delta$ 87.1 ($\underline{C}_5H_5$) $\leftrightarrow$ $\delta$ 5.78 ($C_5\underline{H}_5$); $\delta$ 41.5 ($C_6$) $\leftrightarrow$ $\delta$ 2.09 ($H_{6endo}$), $\delta$ 1.30 ($H_{6exo}$); $\delta$ 41.2 ($C_7$) $\leftrightarrow$ $\delta$ 1.57 ($H_{7exo}$); $\delta$ 22.8 (Me) $\leftrightarrow$ $\delta$ 1.36 (Me). Analysis calculated for $C_{13}H_{16}BCoF_4$: C, 49.10; H, 5.07; found: C, 47.753; H, 4.517.



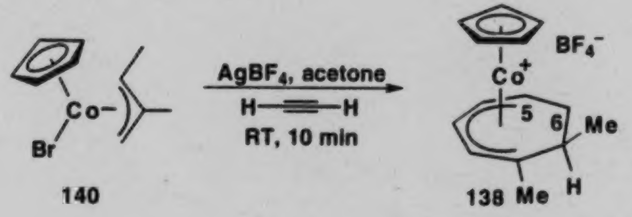
123 136

**($C_5H_5$)Co($\eta^4$-2-Me-$C_4H_5$) (136).** To a solution of CpCo($C_2H_4$)$_2$ (**123**) (0.5351g, 2.970 mmol) in hexanes (25 mL) was added isoprene (1.48 mL, 11 equiv). The solution was stirred overnight at room temperature. The solvent was removed and the residue was extracted with pentane. The pentane extract was filtered through a Celite pad and the solvent was removed. A red oil (0.4831 g, 84%) remained. IR (hexane cast, cm$^{-1}$) 3080 (m), 3038 (s), 2986 (s), 2965 (s), 2944 (s), 2916 (s), 2857 (m), 2728 (w), 1782 (w), 1700 (w), 1675 (w), 1644 (m), 1602 (w), 1559 (w), 1540 (w), 1506 (w), 1454 (m), 1440 (m), 1416 (m), 1375 (s), 1349 (m), 1336 (w), 1258 (w), 1242 (w), 1176 (s), 1149 (w), 1109 (s), 1067 (m), 1051 (m), 1030 (m), 1008 (s), 996 (s), 967 (w), 911 (m), 892 (m), 805 (s), 754 (w), 728 (w), 611 (m), 595 (m), 536 (m), 487 (m); $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 4.83 (dd, J = 8.9, 7.8 Hz, 1H, $H_3$), 4.54 (s, 5H, $C_5\underline{H}_5$), 1.96 (s, 3H, Me), 1.79 (s, 1H, $H_{1s}$), 1.67 (dd, J = 6.5, 1.5 Hz, 1H, $H_{4s}$), -0.38 (s, 1H, $H_{1a}$), -0.50 (dd, J = 9.1, 1.5 Hz, 1H, $H_{4a}$); $^{13}$C NMR (100 MHz, $C_6D_6$) $\delta$ 94.5, 80.2 ($C_5H_5$), 78.6, 34.0, 30.3, 23.4; MS *m/z* calculated for $C_{10}H_{13}Co$ ($M^+$): 192.03493; found: 192.03486 (68 %).



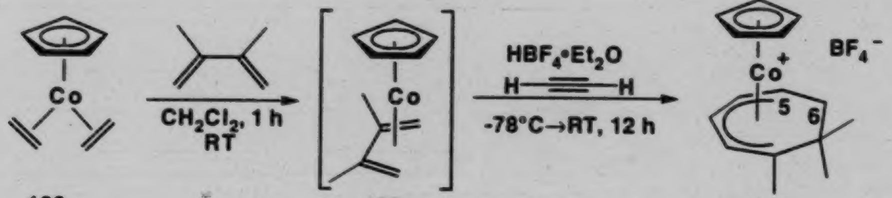
136 140

**($C_5H_5$)Co(1,2-$Me_2$-$C_3H_3$)Br (140).** A solution of CpCo($\eta^4$-isoprene) (**136**) (0.3986 g, 2.074 mmol) in THF (40 mL) was cooled to -78°C. Aqueous HBr (0.235 mL, 48%, 1.0 equiv) was added slowly and the solution was allowed to warm to room temperature over a 12 h period. All volatile material was removed *in vacuo* and the residue was extracted with toluene until no more colored material dissolved. The toluene extracts were filtered through a Celite pad and the solution was reduced to about 5 mL in volume. An equal volume of pentane was added and the solution was cooled to -60°C to crystallize. A small amount of a dark powder was obtained (150 mg, 27%). This material was characterized by $^1$H NMR spectroscopy and used without further purification. $^1$H NMR (400 MHz, $C_6D_6$) δ 4.52 (s, 1H, $H_{3s}$), 4.35 (s, 5H, $C_5\underline{H}_5$), 3.73 (q, $J$ = 7.2 Hz, 1H, $H_1$), 2.80 (s, 1H, $H_{3a}$), 1.40 (d, $J$ = 6.8 Hz, $Me_1$), 1.15 (s, 3H, $Me_2$).



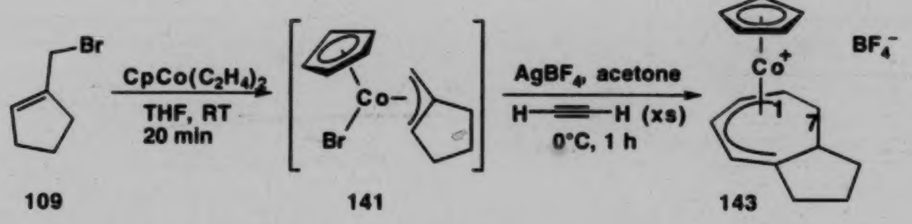
**[($C_5H_5$)Co(1,7-$Me_2C_7H_7$)]$^+$ $BF_4^-$ (138).** To a solution of CpCo(1,2-$Me_2$-$C_3H_3$)Br (**140**) (0.150 g, 0.549 mmol) in reagent grade acetone (30 mL) at 0°C was added silver tetrafluoroborate (0.147 g, 1.38 equiv) and the mixture was stirred for 2 min. Acetylene was then bubbled into the resulting suspension for about 10 min. The suspension was filtered through a Celite pad and the solvent was removed by rotory evaporation. The crude product was purified by flash chromatography on silica gel, eluting with 5% methanol/dichloromethane. A red band was collected and the solvent was removed *in vacuo*, leaving a red-orange residue (0.106 g, 58%). IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3116 (m), 3068 (w), 2969 (m), 2937 (m), 2877 (m), 1716 (w), 1699 (w), 1455 (m), 1431 (m), 1411 (m), 1384 (m), 1375 (m), 1285 (w), 1268 (w), 1052 (s), 1037 (s), 930 (m), 899 (m), 857 (m), 832 (m), 733 (m), 701 (m), 520 (m); $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 7.18 (ddd, $J_{3\text{-}2}$ = $J_{3\text{-}4}$ = 6.6 Hz, $J_{3\text{-}5}$ = 0.9 Hz, 1H, $H_3$), 5.67 (br dd, $J_{4\text{-}5}$ = 7.4 Hz, $J_{4\text{-}3}$ = 6.9 Hz, 1H, $H_4$), 5.55 (d, $J_{2\text{-}3}$ = 7.3 Hz, 1H, $H_2$), 5.45 (s, 5H, $C_5\underline{H}_5$), 5.28 (m, dddd by decoupling, $J_{5\text{-}4}$ = 8.1 Hz, $J_{5\text{-}6endo}$ = 6.0 Hz, $J_{5\text{-}6ex}$ = 4.6 HZ, $J_{5\text{-}3}$ = 1.1 Hz, 1H, $H_5$), 2.06 (ddd, $J_{6endo\text{-}6exo}$ = 14.9 Hz, $J_{6endo\text{-}5}$ = $J_{6endo\text{-}7exo}$ = 5.9 Hz, 1H, $H_{6endo}$), 1.77 (s, 3H, $Me_1$), 1.45 (apparent dq, $J$ = 5.9 Hz, 1H, $H_{7exo}$), 1.37 (d, $J$ = 6.4 Hz, 3H, $Me_7$), 1.15 (dddd, $J_{6exo\text{-}6endo}$ = 14.9 Hz, $J_{6exo\text{-}5}$ = $J_{6exo\text{-}7exo}$ = 4.8 Hz, $J_{6exo\text{-}4}$ = 1.1 Hz, 1H, $H_{6exo}$); $^1$H-$^1$H COSY (400 MHz, $CD_2Cl_2$) δ 7.18 ($H_3$) ↔ δ 5.67 ($H_4$), δ 5.55 ($H_2$), δ 5.28 (w, $H_5$); δ 5.67 ($H_4$) ↔ δ 5.28 (w, $H_5$), δ 1.15 (w, $H_{6exo}$); δ 5.55 ($H_2$) ↔ δ 1.77 (w, $Me_1$); δ 5.28

($H_5$) ↔ δ 2.06 ($H_{6endo}$), δ 1.15 (w, $H_{6exo}$); δ 2.06 ($H_{6endo}$) ↔ δ 1.15 (w, $H_{6exo}$); δ 1.45 ($H_{7exo}$) ↔ δ 1.15 (w, $H_{6exo}$); $^{13}C$ NMR (100 MHz, $CD_2Cl_2$) δ 116.4, 97.1, 95.5, 94.2, 87.9 ($\underline{C}_5H_5$), 83.9, 44.4, 41.6, 28.5, 20.6. Analysis calculated for $C_{14}H_{18}BCoF_4$: C, 50.64; H, 5.46; found: C, 49.506; H, 5.505.



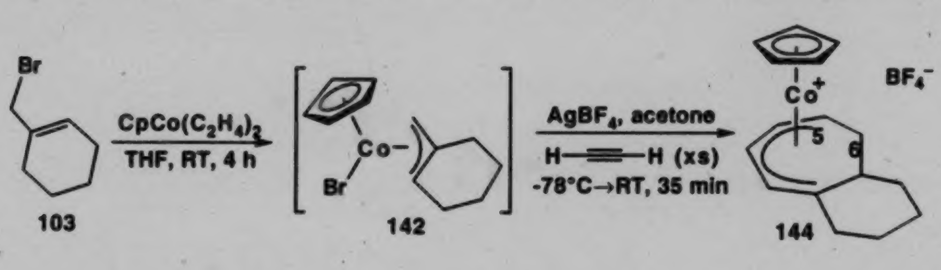
**[($C_5H_5$)Co($\eta^5$-5,6,6-$Me_3C_7H_6$)]$^+$ $BF_4^-$ (139).** In the drybox, a Schlenk flask was charged with ($C_5H_5$)Co($C_2H_4$)$_2$ (**123**) (94.7 mg, 0.526 mmol) and removed to the Schlenk line. Degassed dichloromethane (10 mL) was added and 2,3-dimethylbutadiene (0.1 mL, 2 equiv) was added. The solution was stirred for 1 h until the solution had turned a dark red color, indicating formation of **137**. The solution was cooled to -78 °C and $HBF_4$•$Et_2O$ (0.170 ml, 2 equiv) was added. The solution was stirred 1 min. Acetylene was then bubbled into the solution for 2 min and the reaction flask was allowed to warm slowly to room temperature over a 12 h period. The solution was filtered and all volatile material was removed *in vacuo*. The residue was redissolved in a small amount of dichloromethane and the product was precipitated by the addition of diethyl ether. An additional recrystallization from dichloromethane/diethyl ether gave a light orange powder (64.0 mg, 30%). IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3119 (m), 2968 (m), 1455 (w), 1432 (w), 1413 (m), 1377 (w), 1365 (w), 1054 (s), 923 (w), 860 (m), 519 (m), 451 (m); $^1H$ NMR (360 MHz, $CDCl_3$) δ 7.29 (dd, $J_{3\text{-}2}$ = 6.8 Hz, $J_{3\text{-}4}$ = 5.3 Hz, 1H, $H_3$), 6.15 (dd, $J_{4\text{-}3}$ = 5.3 Hz, $J_{4\text{-}5}$ = 6.6 Hz, 1H, $H_4$), 5.52 (s, 5H, $C_5\underline{H}_5$), 5.26 (d, $J_{2\text{-}3}$ = 6.8 Hz, 1H, $H_2$), 5.13 (m, ddd by decoupling, $J_{5\text{-}6endo}$= 8.4 Hz, $J_{5\text{-}4}$ = 6.6 Hz, $J_{5\text{-}6exo}$ = 5.4 Hz, 1H, $H_5$), 1.87 (s, 3H, $Me_1$), 1.81 (s, 3H, $Me_7$), 1.46 (dd, $J_{6endo\text{-}6exo}$ = 12.6 Hz, $J_{6endo\text{-}5}$ = 8.4 Hz, 1H, $H_{6endo}$), 0.92 (s, 3H, $Me_7$), 0.11 (dd, $J_{6exo\text{-}6endo}$ = 12.7 Hz, $J_{6exo\text{-}5}$ = 5.4 Hz, 1H,

$H_{6exo}$); $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) δ 7.29 ($H_3$) ↔ δ 6.15 ($H_4$), δ 5.26 ($H_2$), δ 5.13 (w, $H_5$); δ 6.15 ($H_4$) ↔ δ 5.13 ($H_5$); δ 5.26 ($H_2$) ↔ δ 1.87 (w, $Me_1$); δ 5.13 ($H_5$) ↔ δ 1.46 ($H_{6endo}$), δ 0.11 ($H_{6exo}$); δ 1.46 ($H_{6endo}$) ↔ δ 0.11 ($H_{6exo}$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 116.3 (s, $C_1$), 98.2 (d, $^1J_{CH}$ = 173.9 Hz, $^2J_{CH}$ = 8.9 Hz, $C_3$), 95.5 (d, $^1J_{CH}$ = 166.3 Hz, $C_2$), 94.6 (d, $^1J_{CH}$ = 174.7 Hz, $C_4$), 88.1 (dt, $^1J_{CH}$ = 183.8 Hz, $^2J_{CH}$ = 6.2 Hz, $\underline{C}_5H_5$), 80.5 (d, $^1J_{CH}$ = 165.4 Hz, $C_5$), 56.1 (s, $C_7$), 40.7 (t, $^1J_{CH}$ = 129.6 Hz, $C_6$), 31.7 (q, $^1J_{CH}$ = 125.9 Hz, $Me_7$), 28.6 (q, $^1J_{CH}$ = 128.0 Hz, $Me_7$), 27.0 (q, $^1J_{CH}$ = 127.7 Hz, $Me_1$); HMQC (300 MHz, $CDCl_3$) δ 98.2 ($C_3$) ↔ δ 7.29 ($H_3$); δ 95.5 ($C_2$) ↔ δ 5.26 ($H_2$); δ 94.6 ($C_4$) ↔ δ 6.15 ($H_4$); δ 88.1 ($\underline{C}_5H_5$) ↔ δ 5.52 ($C_5\underline{H}_5$); δ 80.5 ($C_5$) ↔ δ 5.13 ($H_5$); δ 40.7 ($C_6$) ↔ δ 1.46 ($H_{6endo}$), δ 0.11 ($H_{6exo}$); δ 31.7 ($Me_7$) ↔ δ 1.81 ($Me_7$); δ 28.6 ($Me_7$) ↔ δ 0.92 ($Me_7$); δ 27.0 ($Me_1$) ↔ δ 1.87 ($Me_1$). Analysis calculated for $C_{15}H_{20}BCoF_4$: C, 52.06; H, 5.83; found: C, 52.242; H, 5.512.



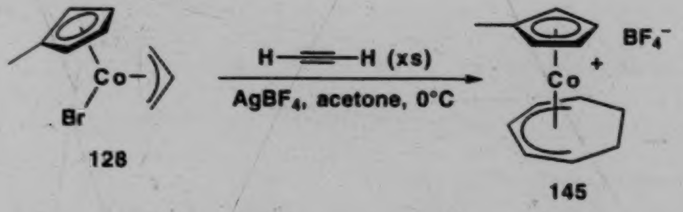
**[($C_5H_5$)Co(1-5η-bicyclo[5.3.0]deca-1,3-dien-5-yl)]$^+$ $BF_4^-$ (143).** To a solution of $C_5H_5Co(C_2H_4)_2$ **(123)** (0.2501 g) in tetrahydrofuran (15 mL) prepared under nitrogen was added 1-(bromomethyl)-1-cyclopentene (**109**) (0.22 g). The solution was stirred for 90 min and then filtered through Celite under nitrogen. All volatile material was removed *in vacuo* and the residue was redissolved in degassed acetone (15 mL). The resulting dark red-purple solution was cooled in an ice bath and silver tetrafluoroborate (excess) was added. Acetylene gas was then bubbled into the resulting slurry for 2 minutes. The slurry was stirred for 1h and then filtered through a Celite pad. Solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel using 5% methanol/dichloromethane as the eluent. A light orange powder (161 mg, 34%) was

obtained. IR (CDCl$_3$ cast, cm$^{-1}$) 3115 (m), 2952 (m), 2868 (m), 2830 (w), 1711 (w), 1450 (m), 1430 (m), 1410 (m), 1349 (w), 1284 (w), 1261 (w), 1176 (w), 1053 (s), 938 (m), 884 (m), 856 (m), 832 (m), 804 (w), 742 (w), 719 (w), 575 (w), 533 (w), 521 (m), 504 (w), 476 (m); $^1$H NMR (300 MHz, CDCl$_3$) δ 7.24 (t, $J_{3\text{-}2} = J_{3\text{-}4} = 6.3$ Hz, 1H, H$_3$), 6.04 (d, $J_{4\text{-}3} = 6.1$ Hz, 1H, H$_4$), 5.49 (s, 5H, C$_5$H$_5$), 5.4-5.3 (m, 2H, H$_{1,2}$), 2.84 (ddd, $J_{7endo\text{-}7exo} = 17.6$, $J_{7endo\text{-}6} = 9.9$ Hz, $J_{7endo\text{-}1} = 3.8$ Hz, 1H, H$_{7endo}$), 2.32 (ddd, $J_{7exo\text{-}7endo} = 17.2$ Hz, $J_{7exo\text{-}6} = 6.1$ Hz, $J_{7exo\text{-}1} = 2.2$ Hz, 1H, H$_{7exo}$), 2.2-1.5 (series of m, 6H, CH$_2$), 0.9-0.7 (m, 1H, H$_6$); $^1$H-$^1$H GCOSY (300 MHz, CDCl$_3$) δ 7.24 (H$_3$) ↔ δ 6.04 (H$_4$), δ 5.35 (H$_2$); δ 5.35 (H$_{1,2}$) ↔ δ 2.84 (H$_{7endo}$), δ 2.32 (H$_{7exo}$); δ 2.84 (H$_{7endo}$) ↔ δ 2.32 (H$_{7exo}$), δ 0.75 (H$_6$); δ 2.32 (H$_{7exo}$) ↔ δ 0.75 (H$_6$). Correlations between methylenes on the small ring are not reported. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 121.7 (s, C$_5$), 96.6 (dd, $^1J_{CH} = 174.8$ Hz, $^2J_{CH} = 9.8$ Hz, C$_3$), 93.2 (d, $^1J_{CH} = 160.3$, C$_{2/1}$), 90.0$^a$ (d, $^1J_{CH} = 163.7$, C$_4$), 87.8$^b$ (d, $^1J_{CH} = 183.25$, $\underline{C}_5$H$_5$), 84.6 (d, $^1J_{CH} = 156.3$, C$_{1/2}$), 48.4 (t, $^1J_{CH} = 130.2$, C$_7$), 42.0 (d, $^1J_{CH} = 130.5$, C$_6$), 40.3 (t, $^1J_{CH} = 129.7$, C$_7$), 33.5 (t, $^1J_{CH} = 130.4$, CH$_2$), 26.5 (t, $^1J_{CH} = 134.7$, CH$_2$). $^a$Signal overlaps with C$_5$H$_5$. $^b$Small $^{2,3}J_{CH}$ are present. $^1$H-$^{13}$C HETCORR (100 MHz, CDCl$_3$) δ 96.6 (C$_3$) ↔ δ 7.24 (H$_3$); δ 93.2 (C$_{1/2}$) ↔ δ 5.3 (H$_{1/2}$); δ 90.0 (C$_4$) ↔ δ 6.04 (H$_4$); δ 87.8 ($\underline{C}_5$H$_5$) ↔ δ 5.49 (C$_5\underline{H}_5$); δ 84.6 (C$_{1/2}$) ↔ δ 5.3 (H$_{1/2}$); δ 48.4 (C$_7$) ↔ δ 2.84 (H$_{7endo}$), δ 2.32 (H$_{7exo}$); δ 42.0 (C$_6$) ↔ δ 0.75 (H$_6$); δ 40.3 (CH$_2$) ↔ δ 2.10 (CH$_2$), δ 1.95 (CH$_2$); δ 33.5 (CH$_2$) ↔ δ 1.70 (CH$_2$), δ 1.45 (CH$_2$); δ 26.5 (CH$_2$) ↔ δ 1.90 (CH$_2$), δ 1.65 (CH$_2$). Analysis calculated for C$_{15}$H$_{18}$BCoF$_4$: C, 52.37; H, 5.27; found: C, 52.345; H, 5.151.



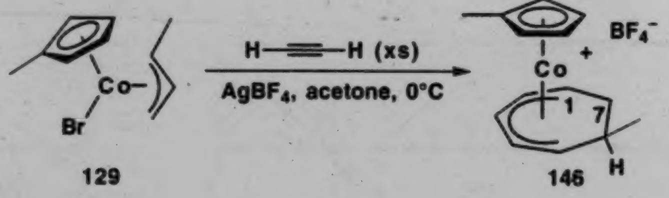
**[(C$_5$H$_5$)Co(1-5η-bicyclo[5.4.0]undeca-1,3-dien-5-yl)]$^+$ BF$_4^-$ (144).** To a Schlenk flask was added (C$_5$H$_5$)Co(C$_2$H$_4$)$_2$ (**123**) (0.4952g, 2.749 mmol) and tetrahydrofuran (25 mL) at -30 °C under nitrogen. 1-(Bromomethyl)-1-cyclohexene (**103**) (0.48 g, 1.0 equiv) was added and the solution allowed to warm to room temperature. After stirring for 4 h, all volatile material was removed *in vacuo* and the residue was redissolved in degassed reagent acetone (25 mL). The solution was cooled to -78 °C and acetylene was bubbled into the solution. $AgBF_4$ (0.589 g, 1.1 equiv) was added and the solution was stirred at -78 °C for 5 min. After 30 min at room temperature the solution was filtered to remove silver residues. The filtrate was taken to dryness and the residue was purified by chromatography (7% methanol-dichloromethane on silica gel). The red fraction was dried and recrystallized from dichloromethane-diethyl ether to give a red-orange powder (0.130 mg, 13%). IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3116 (m), 2935 (s), 2864 (w), 1459 (w), 1445 (w), 1431 (w), 1412 (m), 1274 (s), 1249 (s), 1224 (m), 1157 (m), 1053 (s), 1030 (s), 943 (w), 899 (w), 855 (m), 832 (w), 823 (w), 736 (w), 637 (s), 571 (w), 518 (m), 501 (w), 475 (m); $^1$H NMR (300 MHz, $CD_2Cl_2$) δ 7.19 (ddd, $J_{3\text{-}2} = 6.9$ Hz, $J_{3\text{-}4} = 6.1$ Hz, $J_{3\text{-}5} < 1$ Hz, 1H, $H_3$), 5.86 (dd, $J_{4\text{-}5} = 7.8$ Hz, $J_{4\text{-}3} = 6.3$ Hz, 1H, $H_4$), δ 5.55 (s, 5H, $C_5\underline{H}_5$), δ 5.33 (d, $J_{2\text{-}3} = 7.9$ Hz, 1H, $H_2$), δ 5.24 (m, dddd by decoupling, $J_{5\text{-}4} = J_{5\text{-}6endo} = 7.6$ Hz, $J_{5\text{-}6exo} = 4.5$ Hz, $J_{5\text{-}3} < 1$ Hz, 1H, $H_5$), δ 2.1-1.4 (m, 10H, $H_7$, $H_{6endo}$, $CH_2$), δ 0.75 (m, dddd by decoupling, $J_{6exo\text{-}6endo} = 13.4$ Hz, $J_{6exo\text{-}7} = 6.7$ Hz, $J_{6exo\text{-}5} = 4.5$ Hz, $J_{6\text{-}4} < 1$Hz, 1H, $H_{6exo}$); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) δ 119.1 (s, $C_1$), 97.5 (dd, $^1J_{CH} = 173.2$ Hz, $^2J_{CH} = 9.6$ Hz, $C_3$), 94.3 (br d, $^1J_{CH} = 171.9$ Hz, $C_{2,4}$), 87.2 (dp $^1J_{CH} = 183.6$ Hz, $^2J_{CH} = {}^3J_{CH} = 6.7$ Hz, $\underline{C}_5H_5$), 83.8 (br d, $^1J_{CH} = 159.9$ Hz, $C_5$), 51.8 (d, $^1J_{CH} = 126.3$ Hz, $C_7$), 39.7 (t, $^1J_{CH} = 130.6$ Hz, $CH_2$), 35.4 (t, $^1J_{CH} = 128.8$ Hz, $CH_2$ and $C_6$), 35.3 (t, $^1J_{CH} = 128.2$ Hz, $CH_2$), 25.5 (t, $^1J_{CH} = 127.6$ Hz, $CH_2$), 24.2 (t, $^1J_{CH} = 126.4$ Hz, $CH_2$); $^1$H-$^{13}$C HETCORR (100 MHz, $CD_2Cl_2$) δ 97.5 ($C_3$) ↔ δ 7.19 ($H_3$); δ 94.3 ($C_{2,4}$) ↔ δ 5.86 ($H_4$), δ 5.33 ($H_2$); δ 87.2 ($\underline{C}_5H_5$) ↔ δ 5.55 ($C_5\underline{H}_5$); δ 83.8 ($C_5$) ↔ δ 5.24 ($H_5$); δ 51.8 ($C_7$) ↔ δ 1.65 ($H_7$); δ 39.7 ($CH_2$) ↔ δ 2.20 ($CH_2$), δ 1.90 ($CH_2$); δ 35.3/35.4 ($C_6$, $CH_2$) ↔ δ 2.15 ($H_{6endo}$), δ 1.75 ($CH_2$), δ 0.75 ($C_{6exo}$); δ 25.5 ($CH_2$) ↔ δ 2.00 (s, $CH_2$); δ 24.2

$(CH_2)$ ↔ δ 2.05 $(CH_2)$, δ 1.50 $(CH_2)$. Analysis calculated for $C_{16}H_{20}BCoF_4$: C, 53.67; H, 5.63 found: C, 54.431; H, 5.683.



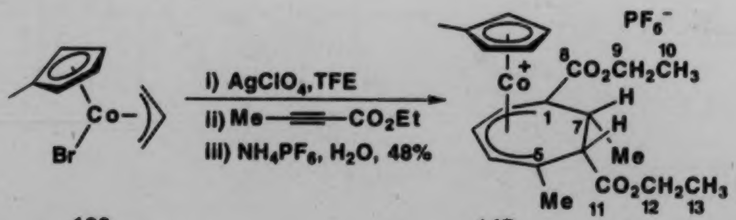
**$[(C_5H_4Me)Co(\eta^5\text{-}C_7H_9]^+ BF_4^-$ (145).** A solution of $(C_5H_4Me)Co(C_3H_5)Br$ **(128)** (0.169 g, 0.652 mmol) in reagent acetone (40 mL) was prepared. Silver tetrafluoroborate (0.177 g, 0.909 mmol, 1.4 equiv) was added. Acetylene was then bubbled slowly into the solution for 10 min. The solution was stirred for 30 min, then filtered to remove silver salts and the solvent was removed *in vacuo*. The residue was purified by flash chromatography on silica gel, using 5% methanol/dichloromethane as the eluent. The product was recrystallized from dichloromethane/diethyl ether to give a red powder (152 mg, 73%). IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3109 (w), 2938 (w), 2876 (w), 1480 (w), 1455 (w), 1364 (w), 1054 (s), 1037 (s), 978 (w), 953 (w), 931 (w), 920 (w), 881 (w), 854 (w), 835 (w), 818 (w), 733 (w), 521 (w), 509 (w), 483 (w); $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.24 (dd, $J_{3\text{-}2} = J_{3\text{-}4} = 6.3$ Hz, 1H, $H_3$), 5.59 (dd, $J_{2\text{-}1} = 8.7$ Hz, $J_{2\text{-}3} = 6.6$ Hz, 2H, $H_{2/4}$), 5.53 (t, $J = 2.1$ Hz, 2H, Cp'), 5.47 (t, $J = 2.1$ Hz, 2H, Cp'), 5.35-5.25 (m, 2H, $H_{1/5}$), 2.50 -2.40 (m, 2H, $H_{6endo/7endo}$), 1.99 (s, 3H, Cp' Me), 1.3-1.1 (m, 2H, $H_{6exo/7exo}$); $^1H$-$^1H$ GCOSY (300 MHz, $CDCl_3$) δ 7.24 ($H_3$) ↔ δ 5.59 ($H_{2/4}$), δ 5.3 (w, $H_{1/5}$); δ 5.59 ($H_{2/4}$) ↔ δ 5.3 ($H_{1/5}$); δ 5.3 ($H_{1/5}$) ↔ δ 2.45 ($H_{6endo/7endo}$), δ 1.2 ($H_{6exo/7exo}$); δ 2.45 ($H_{6endo/7endo}$) ↔ δ 1.2 ($H_{6exo/7exo}$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 104.9 (s, Cp' ring quaternary), 100.6 (dt, $^1J_{CH} = 173.1$ Hz, $^2J_{CH} = 9.5$ Hz, $C_3$), 95.6 (d, $^1J_{CH} = 169.9$ Hz, $C_{2/4}$), 89.3 (dd, $^1J_{CH} = 156.9$ Hz, $^2J_{CH} = 8.5$ Hz, $C_{1/5}$), 87.1 (d, $^1J_{CH} = 181.7$ Hz, Cp'), 85.9 (d, $^1J_{CH} = 183.2$ Hz, long range $J_{CH}$ observed, Cp'), 34.1 (t, $^1J_{CH} = 131.2$ Hz, $C_{6/7}$), 12.9 (q, $^1J_{CH} = 129.5$ Hz, Cp' Me); $^1H$-$^{13}C$ HETCORR (100 MHz, $CDCl_3$) δ 100.6 ($C_3$) ↔ δ 7.24 ($H_3$);

δ 95.6 ($C_{2/4}$) ↔ δ 5.59 ($H_{2/4}$); δ 89.3 ($C_{1/5}$) ↔ δ 5.3 ($H_{1/5}$); δ 87.1 (Cp') ↔ δ 5.53 (Cp'); δ 85.9 (Cp') ↔ δ 5.47 (Cp'); δ 34.1 ($C_{6/7}$) ↔ δ 2.45 ($H_{6endo/7endo}$), δ 1.3 ($H_{6exo/7exo}$); δ 12.9 (Cp' Me) ↔ δ 1.99 (Cp' Me). Analysis calculated for $C_{13}H_{16}BCoF_4$: C, 49.10; H, 5.07; found: C, 49.349; H, 5.092.



**[($C_5H_4Me$)Co($\eta^5$-6-Me-$C_7H_8$]$^+$ $BF_4^-$ (146).** A solution of ($C_5H_4Me$)Co(1-Me-$C_3H_4$)Br (**129**) (0.128 g, 0.469 mmol) in reagent acetone (15 mL) was prepared. Silver tetrafluoroborate (about 1.5 equiv) was added. Acetylene was then bubbled slowly into the solution for 10 min. The solution was filtered to remove silver residues and the solvent was removed *in vacuo*. The residue was chromatographed on silica gel, using 5% methanol/dichloromethane. The red product was recrystallized from dichloromethane/diethyl ether to give an orange-red solid (51.0 mg, 33%). IR ($CH_2Cl_2$ cast, cm $^{-1}$) 3115 (w), 2976 (w), 2937 (w), 2880 (w), 1479 (m), 1459 (w), 1449 (m), 1409 (w), 1388 (w), 1376 (m), 1367 (w), 1359 (w), 1320 (w), 1300 (w), 1120 (w), 1107 (w), 1042 (m), 1011 (w), 929 (w), 900 (w), 877 (s), 833 (s), 777 (w), 740 (w), 557 (s), 499 (w), 480 (w); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.22 (dd, $J_{3\text{-}2} = J_{3\text{-}1} = 6.6$ Hz, 1H, $H_3$), 5.6-5.4 (m, 6H, $H_2$, $H_4$, 4 Cp'), 5.14 (ddd, $J_{1\text{-}2} = 9.3$ Hz, $J_{1\text{-}7endo} = 6.0$ Hz, $J_{1\text{-}7exo} = 3.6$ Hz, 1H, $H_1$), 4.95 (dd, $J_{5\text{-}4} = 8.7$ Hz, $J_{5\text{-}6} = 3.6$ Hz, 1H, $H_5$), 2.06 (ddd, $J_{7endo\text{-}7exo} = 15.3$ Hz, $J_{7endo\text{-}1} = J_{7endo\text{-}6} = 5.7$ Hz, 1H, $H_{7endo}$), 1.94 (s, 3H, Cp' Me), 1.52-1.48 (m, 1H, $H_6$), 1.35 (dddd, $J_{7exo\text{-}7endo} = 15.3$ Hz, $J_{7exo\text{-}1} = J_{7exo\text{-}6} = 3.9$ Hz, $J = 1.2$ Hz, 1H, $H_{7exo}$), 1.32 (d, $J = 6.6$ Hz, 3H, $Me_6$); $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) δ 7.22 ($H_3$) ↔ δ 5.50 ($H_{2,4}$); δ 5.50 ($H_{2,4,Cp'}$) ↔ δ 5.14 ($H_1$), δ 4.95 ($H_5$), δ 1.32 (w, $Me_6$), δ 1.94 (w, Cp' Me); δ 5.14 ($H_1$) ↔ δ 2.06 ($H_{7endo}$), 1.32 ($Me_6$); δ 4.95 ($H_5$) ↔ δ 1.50 ($H_6$); δ

2.06 ($H_{7endo}$) ↔ δ 1.50 ($H_6$), δ 1.35 ($H_{7exo}$), δ 1.32 ($Me_6$); δ 1.50 ($H_6$) ↔ δ 1.32 ($Me_6$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 104.9 (s, Cp' ring quaternary), 100.8 (dt, $^1J_{CH}$ = 173.4 Hz, $^2J_{CH}$ = 9.3 Hz, $C_3$), 95.9[a] (d, $^1J_{CH}$ = 170.7 Hz, Cp'), 95.0[a] (d, $^1J_{CH}$ = 154.7 Hz, $C_5$), 94.1 (d, $^1J_{CH}$ = 170.9 Hz, Cp'), 87.3[b] (d, $^1J_{CH}$ = 157.5 Hz, $C_{2/4}$), 87.1[b] (d, $^1J_{CH}$ = 157.5 Hz, $C_{2/4}$), 86.9 (d, $^1J_{CH}$ = 176.3 Hz, $C_1$), 85.8[c] (d, $^1J_{CH}$ = 183.2 Hz, Cp'), 85.7[c] (d, $^1J_{CH}$ = 183.2 Hz, Cp'), 42.2 (t, $^1J_{CH}$ = 128.6 Hz, $C_7$), 40.4 (t, $^1J_{CH}$ = 127.3 Hz, $C_6$), 22.7 (q, $^1J_{CH}$ = 126.1 Hz, $Me_6$), 13.0 (q, $^1J_{CH}$ = 129.9 Hz, Cp' Me). [a,b,c] indicate pairs of overlapping signals in the gated decoupled spectrum. $C_2$ and $C_4$ are distinguished from Cp' ligand based on magnitude of $^1J_{CH}$. $^1H$-$^{13}C$ HETCORR (100 MHz, $CDCl_3$) δ 100.8 ($C_3$) ↔ δ 7.22 ($H_3$); δ 95.9 (Cp') ↔ δ 5.5 (Cp'); δ 95.0 ($C_5$) ↔ δ 4.95 ($H_5$); δ 94.1 (Cp') ↔ δ 5.5 (Cp'); δ 87.3 ($C_{2/4}$) ↔ δ 5.50 ($H_{2/4}$); δ 87.1 ($C_{2/4}$) ↔ δ 5.50 ($H_{2/4}$); δ 86.9($C_1$) ↔ δ 5.14 ($H_1$); δ 85.8 (Cp') ↔ δ 5.50 (Cp'); δ 85.7 (Cp') ↔ δ 5.50 (Cp'); δ 42.2 ($C_7$) ↔ δ 2.06 ($H_{7endo}$), δ 1.35 ($H_{7exo}$); δ 22.7 ($Me_6$) ↔ δ 1.32 ($Me_6$); δ 13.0 (Cp' Me) ↔ δ 1.94 (Cp' Me). Even after several recrystallizations from dichloromethane-diethyl ether, a satisfactory analysis was not obtained. MS *m/z* calculated for $C_{14}H_{17}Co$ ($M^+$): 244.06622; found: 244.06595 (100 %).



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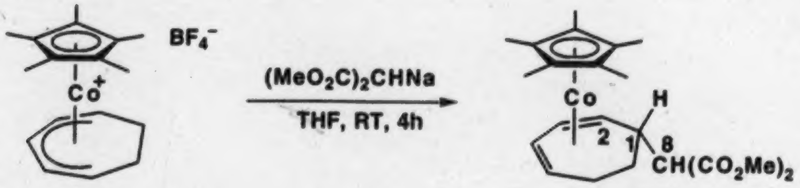
**[($C_5H_4Me$)Co($\eta^5$-5,7-$Me_2$-1,6-($CO_2Et$)$_2C_7H_5$]$^+$ $PF_6^-$ (147).** A solution of ($C_5H_4Me$)Co ($\eta^3$-$C_3H_5$)(Br) (**128**) (100 mg, 0.386 mmol) was prepared in 2,2,2-trifluoroethanol (5 mL). To this solution was added silver perchlorate (113 mg, 1.3 equiv) and the solution was stirred 10 min under nitrogen before ethyl 2-butynoate (0.5 mL, excess) was added. The solution was stirred under nitrogen for 12 h and filtered to remove silver residues. All volatile components were removed *in vacuo* and the residue flash chromatographed on silica gel, using 5% methanol-dichloromethane. A deep red liquid (88 mg, 48%) was obtained. The hexafluorophosphate salt was prepared by precipitation from aqueous solution using $NH_4PF_6$. IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3100 (w), 2980 (m), 2936 (w), 1727 (s), 1708 (s), 1479 (w), 1451 (m), 1379 (w), 1367 (m), 1280 (m), 1236 (s), 1179 (m), 1162 (m), 1096 (s), 1028 (m), 921 (w), 899 (w), 865 (w), 624 (m), 469 (w); $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.46 (dd, $J_{3-4} = 7.2$ Hz, $J_{3-2} = 6.9$ Hz, 1H, $H_3$), 6.38 (d, $J_{2-3} = 6.9$ Hz, 1H, $H_2$), 5.98 (d, $J_{4-3} = 7.2$ Hz, 1H, $H_4$), 5.62 (br s, 1H, Cp'), 5.54 (br s, 1H, Cp'), 5.28 (br s, 1H, Cp'), 5.21 (br s, 1H, Cp'), 4.35 (q, $J_{9-10} = 7.1$ Hz, 2H, $H_9$), 4.03 (q, $J_{12-13} = 7.1$ Hz, 2H, $H_{12}$), 3.97 (d, $J_{6-7} = 9.6$ Hz, 1H, $H_6$), 3.54 (dq, $J_{7-6} = 9.6$ Hz, $J_{7\text{-}Me} = 7.2$ Hz, 1H, $H_7$), 2.05 (s, 3H, Cp' Me), 2.00 (s, 3H, $Me_5$), 1.43 (t, $J_{10-9} = 7.1$ Hz, 3H, $H_{10}$), 1.19 (t, $J_{13-12} = 7.1$ Hz, 3H, $H_{13}$), 0.40 (d, $J = 7.2$ Hz, 3H, $Me_7$); $^1H$-$^1H$ GCOSY (300 MHz, $CDCl_3$) δ 7.46 ($H_3$) ↔ δ 6.38 ($H_2$), δ 5.98 ($H_4$); δ 5.62 (Cp') ↔ δ 5.54 (Cp'), δ 5.28 (Cp'), δ 5.21 (Cp'); δ 5.54 (Cp') ↔ δ 5.28 (Cp'), δ 5.21 (Cp'); δ 5.28 (Cp') ↔ δ 5.21 (Cp'); δ 4.35 ($H_9$) ↔ δ 1.43 ($H_{10}$); δ 4.03 ($H_{12}$) ↔ δ 1.19 ($H_{13}$); δ 3.97 ($H_6$) ↔ δ 3.54 ($H_7$); δ 3.54 ($H_7$) ↔ δ 0.40 ($Me_7$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 170.8 (s, $C_8$), 167.3 (s, $C_{11}$), 107.3 (s, Cp' ring quaternary), 105.8 (s, $C_5$), 98.8 (d, $^1J_{CH} = 176.6$ Hz, $C_3$), 98.0 (d, $^1J_{CH} = 169.3$ Hz, $C_4$), 94.8 (d, $^1J_{CH} = 180.7$ Hz, $C_2$), $90.9^a$ (d, $^1J_{CH} = 185$ Hz, Cp'), $90.6^{a,b}$ (d, $^1J_{CH} = 185$ Hz, Cp'), 89.9 (d, $^1J_{CH} = 180.4$ Hz, Cp'), $88.8^b$ (d, $^1J_{CH} = 186.3$ Hz, Cp'), 85.7 (s, $C_1$), 62.8 (t, $^1J_{CH} = 149.9$ Hz, $C_9$), 61.9 (d, $^1J_{CH} = 135.8$ Hz, $C_6$), 61.6 (t, $^1J_{CH} = 146.1$ Hz, $C_{12}$), 37.7 (d, $^1J_{CH} = 136.4$ Hz, $C_7$), 30.7 (q, $^1J_{CH} = 130.1$ Hz, $Me_5$), 19.2 (q, $^1J_{CH} = 129.1$ Hz, $Me_7$), 14.4 (q, $^1J_{CH} = 126.3$ Hz, $C_{10}$), 14.1 (q, $^1J_{CH} = 127.4$ Hz, $C_{13}$), 12.0 (q, $^1J_{CH} = 129.7$ Hz, Cp' Me). $^{a,b}$ Denote pairs of overlapping signals in the gated decoupled spectrum. HMQC (300 MHz, $CDCl_3$) δ 98.8 ($C_3$) ↔ δ 7.46 ($H_3$); δ 98.0 ($C_4$) ↔ δ 5.98 ($H_4$); δ 94.8 ($C_2$) ↔ δ 6.38 ($H_2$); δ 90.9 (Cp') ↔ δ 5.21 (Cp'); δ 90.6 (Cp') ↔ δ 5.62 (Cp'); δ 89.9 (Cp') ↔ δ 5.28 (Cp'); δ 88.8 (Cp') ↔ δ 5.54 (Cp'); δ 62.8 ($C_9$) ↔ δ 4.35 ($H_9$); δ 61.9 ($C_6$) ↔ δ 3.97 ($H_6$); δ 61.6 ($C_{12}$) ↔ δ 4.03 ($H_{12}$); δ 37.7 ($C_7$) ↔ δ 3.54 ($H_7$); δ 30.7 ($Me_5$) ↔ δ 2.00 ($Me_5$); δ 19.2 ($Me_7$) ↔ δ

0.40 (Me$_7$); δ 14.4 (C$_{10}$) ↔ δ 1.43 (H$_{10}$); δ 14.1 (C$_{13}$) ↔ δ 1.19 (H$_{13}$); δ 12.0 (Cp' Me) ↔ δ 2.05 (Cp' Me); HMBC (300 MHz, $CDCl_3$) δ 170.8 (C$_8$) ↔ δ 6.38 (H$_2$), δ 4.35 (H$_9$); δ 167.3 (C$_{11}$) ↔ δ 4.03 (H$_{12}$), δ 3.97 (H$_6$); δ 107.3 (Cp' ring quaternary) ↔ δ 5.62 (Cp'), δ 5.54 (Cp'), δ 5.28 (Cp'), δ 5.21 (Cp'), δ 2.05 (Cp' Me); δ 105.8 (C$_5$) ↔ δ 7.46 (H$_3$), δ 3.97 (H$_6$), δ 3.54 (H$_7$), δ 2.00 (Me$_5$); δ 98.0$^a$ (C$_3$) ↔ δ 6.38 (H$_2$), δ 3.97 (H$_6$), δ 2.00 (Me$_5$); δ 94.8 (C$_2$) ↔ δ 7.46 (w, H$_3$), δ 5.98 (H$_4$), δ 3.54 (H$_7$); δ 90.9/90.6 (Cp') ↔ δ 5.62 (Cp'), δ 5.54 (Cp'), δ 5.28 (Cp'), δ 5.21 (Cp'), δ 2.05 (Cp' Me); δ 89.9 (Cp') ↔ δ 5.62 (Cp'), δ 5.54 (Cp'), δ 5.21 (Cp'), δ 2.05 (Cp' Me); δ 88.8 (Cp') ↔ δ 5.62 (Cp'), δ 5.28 (Cp'), δ 5.21 (Cp'); δ 85.7 (C$_1$) ↔ δ 7.46 (H$_3$), δ 3.97 (H$_6$), δ 3.54 (H$_7$), δ 0.40 (Me$_7$); δ 62.8 (C$_9$) ↔ δ 1.43 (H$_{10}$); δ 61.6/61.9 (C$_{6/12}$) ↔ δ 5.98 (H$_4$), δ 2.00 (Me$_5$), δ 1.19 (H$_{13}$), δ 0.40 (Me$_7$); δ 37.7 (C$_7$) ↔ δ 6.38 (H$_2$), δ 3.97 (H$_6$), δ 0.40 (Me$_7$); δ 30.7 (Me$_5$) ↔ δ 5.98 (H$_4$), δ 3.97 (H$_6$); δ 19.2 (Me$_7$) ↔ δ 3.97 (H$_6$), δ 3.54 (H$_7$); 14.4/14.1 (C$_{10/13}$) ↔ δ 4.35 (H$_9$), δ 4.03 (H$_{12}$), δ 1.43 (H$_{10}$), δ 1.19 (H$_{13}$). $^a$C$_3$ and C$_4$ signals are not resolved. MS *m/z* calculated for $C_{21}H_{28}CoO_4$ ($M^+$): 403.13196; found: 403.13368 (2.56%). Analysis calculated for $C_{21}H_{28}CoF_6O_4P$: C, 46.00; H, 5.15; found: C, 45.508; H, 4.56.

## Chapter 3 Experimental Section



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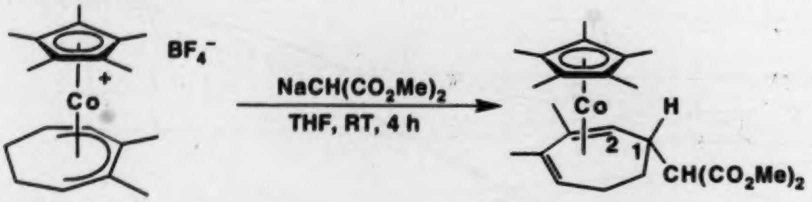
**Pentamethylcyclopentadienyl[dimethyl (2-5η–cyclohepta-2,4-dienyl)malonate] cobalt. [($C_5Me_5$)Co($\eta^4$-1-(bis(carbomethoxy)methyl)cyclohepta-2,4-diene)] (192).** In the drybox, a solution of [($C_5Me_5$)Co-$\eta^5$-$C_7H_9$]$^+$ $BF_4^-$ (**99**-$BF_4$) (115 mg, 0.307 mmol) in tetrahydrofuran (10 mL) was prepared. To this orange solution, solid sodium dimethylmalonate (104 mg, 0.672 mmol, 2.2 equiv) was added and the solution was stirred for 4 h. A gradual color change to deep red was observed. At the end of 4 h, the solvent was removed *in vacuo* and the residue extracted with pentane until the extracts were colorless. The combined extracts were filtered through a Celite pad and the solvent was removed *in vacuo*, leaving a dark red solid (91.3 mg, 71%). IR (hexane cast, $cm^{-1}$) 2995 (m), 2952 (s), 2916 (s), 2849 (m), 1757 (s), 1434 (s), 1381 (m), 1324 (m), 1292 (m), 1261 (s), 1246 (m), 1230 (m), 1213 (m), 1191 (m), 1147 (s), 1030 (m); $^1$H NMR (360 MHz, $C_6D_6$) δ 4.07 (dd, $J_{3\text{-}4}$ = 4.5 Hz, $J_{3\text{-}2}$ = 6.8 Hz, 1H, $H_3$), 4.01 (distorted dd, $J_{4\text{-}3}$ = 4.7, $J_{4\text{-}5}$ = 6.9 Hz, 1H, $H_4$), 3.43 (s, 3H, $CO_2\underline{Me}$), 3.35 (s, 3H, $CO_2\underline{Me}$), 3.34 (d, $J_{8\text{-}1}$ = 8.2 Hz, 1H, $H_8$), 2.49 (dddd, $J_{1\text{-}7exo}$ = 11.9 Hz, $J_{1\text{-}8}$ = 8.3 Hz, $J_{1\text{-}7endo}$ = 3.5 Hz, $J_{1\text{-}2}$ = 1.7 Hz, 1H, $H_1$), 2.21 (br d, $J_{2\text{-}3}$ = 6.7 Hz, 1H, $H_2$), 2.16 (br t, $J_{obs}$ = 6.2 Hz, 1H, $H_5$), 1.72 (s, 15H, $C_5\underline{Me_5}$), 1.7-1.6 (m, 1H, $H_{6exo}$), 1.48 (dddd, $J_{6endo\text{-}6exo}$ = 13 Hz, $J_{6endo\text{-}7exo}$ = 12.8 Hz, $J_{6endo\text{-}7endo}$ = 3.5 Hz, $J_{6endo\text{-}5}$ = 1.6 Hz, 1H, $H_{6endo}$), 1.34 (br d, $J_{7endo\text{-}7exo}$ = 12.7 Hz, 1H, $H_{7endo}$), 0.84 (qd, $J_{7exo\text{-}7endo}$ = $J_{7exo\text{-}6endo}$ = $J_{7exo\text{-}1}$ = 12.6 Hz, $J_{7exo\text{-}6exo}$ = 3.8 Hz, 1H, $H_{7exo}$); $^1$H-$^1$H COSY (400 MHz, $C_6D_6$) δ 4.06 ($H_3$) ↔ δ 4.01 ($H_4$), δ 2.21 ($H_2$), δ 2.16 ($H_5$); δ 4.01 ($H_4$) ↔ δ 2.21 ($H_2$), δ 2.16 ($H_5$); δ 3.34 ($H_8$) ↔ δ

2.49 ($H_1$); δ 2.49 ($H_1$) ↔ δ 2.21 ($H_2$), δ 1.48 ($H_{6endo}$) δ 1.34 ($H_{7endo}$); δ 2.16 ($H_5$) ↔ δ 1.65 ($H_{6exo}$), δ 1.48 ($H_{6endo}$) δ 1.34 ($H_{7endo}$); δ 1.65 ($H_{6exo}$) ↔ δ 1.48 ($H_{6endo}$), δ 0.84 ($H_{7exo}$); δ 1.48 ($H_{6endo}$) ↔ δ 1.34 ($H_{7endo}$), δ 0.84 ($H_{7exo}$); δ 1.34 ($H_{7endo}$) ↔ δ 0.84 ($H_{7exo}$); $^{13}$C NMR (75 MHz, $C_6D_6$) δ 169.1$^a$ (m, $\underline{C}O_2Me$), 168.7$^a$ (m, $\underline{C}O_2Me$), 89.9 (s, $C_5\underline{Me}_5$), 82.1$^b$ (d, $^1J_{CH}$ = 162.2 Hz, $C_4$), 80.0$^b$ (d, $^1J_{CH}$ = 158.5 Hz, $C_3$), 60.2 (d, $^1J_{CH}$ = 133.3 Hz, $C_8$), 53.0 (d, $^1J_{CH}$ = 145.8 Hz, $C_5$), 52.6 (d, $^1J_{CH}$ = 145.0 Hz, $C_2$), 51.6 (q, $^1J_{CH}$ = 146.8 Hz, $CO_2\underline{Me}$), 39.8 (d, $^1J_{CH}$ = 133.5 Hz, $C_1$), 28.9 (t, $^1J_{CH}$ = 125 Hz, $C_6$), 27.9 (t, $^1J_{CH}$ = 126 Hz, $C_7$), 9.5 (q, $^1J_{CH}$ = 126.1 Hz, $C_5\underline{Me}_5$). $^a$Small unresolved $^2J_{CH}$ and $^3J_{CH}$ complicate the signal. $^b$In the gated spectrum, these two signals overlap. $^1$H-$^{13}$C HETCORR (100 MHz, $C_6D_6$) δ 82.1 ($C_4$) ↔ δ 4.01 ($H_4$); δ 80.0 ($C_3$) ↔ δ 4.07 ($H_3$); δ 60.2 ($C_8$) ↔ δ 3.34 ($H_8$); δ 53.0 ($C_5$) ↔ δ 2.16 ($H_5$); δ 52.6 ($C_2$) ↔ δ 2.21 ($H_2$); δ 51.6 ($CO_2\underline{Me}$) ↔ δ 3.43-3.35 ($CO_2\underline{Me}$); δ 39.8 ($C_1$) ↔ δ 2.49 ($H_1$); δ 28.9 ($C_6$) ↔ δ 1.65 ($H_{6exo}$), δ 1.48 ($H_{6endo}$); δ 27.9 ($C_7$) ↔ δ 1.34 ($H_{7endo}$), δ 0.84 ($H_{7exo}$); δ 9.5 ($C_5\underline{Me}_5$) ↔ δ 1.72 ($C_5\underline{Me}_5$). MS *m/z* calculated for $C_{22}H_{31}CoO_4$ ($M^+$): 418.15543; found: 418.15411 (76%).



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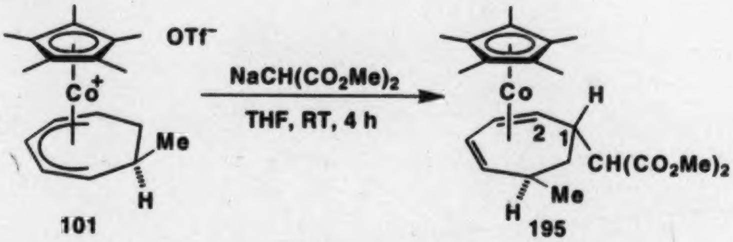
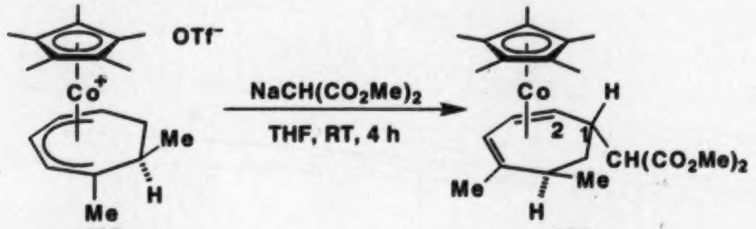
**Pentamethylcyclopentadienyl[dimethyl (2-5-η-3,4-dimethylcyclohepta-2,4-dienyl)malonate]cobalt. [($C_5Me_5$)Co(η$^4$-1-(bis(carbomethoxy)methyl)-3,4-dimethylcyclohepta-2,4-diene)] (194).** In the drybox, a solution of [($C_5Me_5$)Co-η$^5$-3,4-$Me_2$-$C_7H_7$]$^+$ $BF_4^-$ (**193**) (134.8 mg, 0.3351 mmol) in tetrahydrofuran (12 mL) was prepared. To this orange solution, solid sodium dimethylmalonate (86.3 mg, 0.560 mmol, 1.7 equiv) was added and the solution was stirred for 4 h. No obvious color change was observed. At the end of 4 h, the solvent was removed *in vacuo* and the residue extracted with pentane until the extracts were colorless. The combined extracts were filtered through a Celite pad and the solvent was removed *in vacuo*, leaving 108.6 mg (73%) of an orange solid. Crystals suitable for an X-ray diffraction analysis were grown from a saturated solution of pentane cooled slowly from room temperature to -35 °C. For full data on this crystal structure, request report # JMS9609 from the Structure Determination Laboratory at the University of Alberta Department of Chemistry. IR (hexane cast, $cm^{-1}$) 2978 (m), 2908 (m), 1753 (s), 1734 (s), 1433 (s), 1376 (m), 1285 (m), 1250 (s), 1197 (m), 1149 (s), 1027 (m); $^1H$ NMR (400 MHz, $C_6D_6$) δ 3.43 (s, 3H, $CO_2\underline{Me}$), 3.27 (s, 3H, $CO_2\underline{Me}$), 3.32 (d, $J_{8\text{-}1}$ = 7.4 Hz, 1H, $H_8$), 2.31 (dddd, $J_{1\text{-}7exo}$ = 11.1 Hz, $H_{1\text{-}8}$ = 7.4 Hz, $J_{1\text{-}7endo}$ = 3.6 Hz, $J_{1\text{-}2}$ = 1.3 Hz, 1H, $H_1$), 2.05-1.95 (m, 2H, $H_{2,5}$), 1.79 (s, 3H, $Me_3$), 1.72 (s, 3H, $Me_2$), 1.68 (s, 15H, $C_5\underline{Me_5}$), 1.75-1.65 (m, 1H, obscured by $C_5\underline{Me_5}$, $H_{6exo}$), 1.40-1.31 (m, 1H, $H_{6endo}$), 1.31-1.25 (m, 1H, $H_{7endo}$), 0.69 (qd, $J_{7exo\text{-}1}$ = $J_{7exo\text{-}7endo}$ = $J_{7exo\text{-}6endo}$ = 12.0 Hz, $J_{7exo\text{-}6exo}$ = 3.5 Hz, 1H, $H_{7exo}$); $^1H$-$^1H$ COSY (400 MHz, $C_6D_6$) δ 3.32 ($H_8$) ↔ δ 2.31 ($H_1$); δ 2.31 ($H_1$) ↔ δ 2.0 ($H_{2,5}$), δ 1.3 ($H_{7endo}$), 0.69 ($H_{7exo}$); δ 2.0 ($H_{2,5}$) ↔ δ 1.70 ($H_{6exo}$), δ 1.3 ($H_{7endo}$); δ 1.3 ($H_{7endo}$) ↔ δ 0.69 ($H_{7exo}$); $^{13}C$ NMR (100 MHz, $C_6D_6$) δ 169.2$^a$ (m, $\underline{C}O_2Me$), 168.9$^a$ (m, $\underline{C}O_2Me$), 89.4 (s, $\underline{C_5}Me_5$), 88.7 (s, $C_{3/4}$), 87.3 (s, $C_{3/4}$), 60.0 (d, $^1J_{CH}$ = 131.6 Hz, $C_8$), 53.7$^b$ (br d, $^1J_{CH}$ = 141 Hz, $C_{2/5}$), 53.6$^b$ (br d, $^1J_{CH}$ = 141 Hz, $C_{2/5}$), 51.5 (q, $^1J_{CH}$ = 146.3 Hz, $CO_2\underline{Me}$), 40.1 (d, $^1J_{CH}$ = 131.7 Hz, $C_1$), 28.5 (t, $^1J_{CH}$ = 124.4 Hz, $C_6$), 28.0 (t, $^1J_{CH}$ = 124.6 Hz, $C_7$), 19.1 (qd, $^1J_{CH}$ = 125.2 Hz, $^2J_{CH}$ = 4.6 Hz, $Me_3$), 18.5 (qd, $^1J_{CH}$ = 125.0 Hz, $^2J_{CH}$ = 4.3 Hz, $Me_2$), 9.3 (q, $^1J_{CH}$ = 125.0 Hz, $C_5\underline{Me_5}$). $^a$Small unresolved $^2J_{CH}$ and $^3J_{CH}$ complicate the signal. $^b$Signals overlap in gated spectrum. $^1H$-$^{13}C$ HETCORR (100 MHz, $C_6D_6$) δ 60.0 ($C_8$) ↔ δ 3.32 ($H_8$); δ 53.7/53.6 ($C_{2/5}$) ↔ δ 2.0 ($H_{2/5}$); δ 51.5 ($CO_2\underline{Me}$) ↔ δ 3.43 ($CO_2\underline{Me}$), δ 3.37 ($CO_2\underline{Me}$); δ 40.1 ($C_1$) ↔ δ 2.31 ($H_1$); δ 28.5 ($C_6$) ↔ δ 1.70 ($H_{6exo}$), δ 1.36 ($H_{6endo}$); δ 28.0 ($C_7$) ↔ δ 1.25 ($H_{7endo}$), δ 0.69 ($H_{7exo}$); δ 19.1 ($Me_3$) ↔ δ 1.79 ($Me_3$); δ 18.5 ($Me_2$) ↔ δ 1.72 ($Me_2$); δ 9.3

($C_5\underline{Me}_5$) ↔ δ 1.68 ($C_5\underline{Me}_5$). MS *m/z* calculated for $C_{24}H_{35}CoO_4$ ($M^+$): 446.18674; found: 446.18633 (59%). Analysis calculated for $C_{24}H_{35}CoO_4$: C, 64.56; H, 7.90; found: C, 64.655; H, 8.041.



**Pentamethylcyclopentadienyl[dimethyl-(2-5-η-6-methylcyclohepta-2,4-dienyl)malonate]cobalt. [($C_5Me_5$)Co($\eta^4$-1-(bis(carbomethoxy)methyl)-6-methylcyclohepta-2,4-diene)] (195).** In the drybox, a solution of [($C_5Me_5$)Co($\eta^5$-6-Me-$C_7H_8$]$^+$ $OTf^-$ (**101**) (32.0 mg, 0.071 mmol) in tetrahydrofuran (10 mL) was prepared. To this red solution, solid sodium dimethylmalonate (86.5 mg, 0.561 mmol, 7.9 equiv) was added and the solution was stirred for 4 h. The color gradually darkened. At the end of 4 h, the solvent was removed *in vacuo* and the residue extracted with pentane until the extracts were colorless. The combined extracts were filtered through a Celite pad and the solvent was removed *in vacuo*, leaving a deep red oil (19.3 mg, 63%). IR (hexane cast, $cm^{-1}$) 2950 (m), 2910 (m), 1755 (s), 1735 (s), 1433 (m), 1259 (s), 1221 (m), 1192 (m), 1151 (s), 1093 (m), 1026 (s), 799 (m); $^1H$ NMR (300 MHz, $C_6D_6$) δ 3.98 (dd, $J_{3\text{-}2}$ = 7.0 Hz, $J_{3\text{-}4}$ = 4.7 Hz, 1H, $H_3$), 3.85 (dd, $J_{4\text{-}5}$ = 7.0 Hz, $J_{4\text{-}3}$ = 4.6 Hz, 1H, $H_4$), 3.43 (s, 3H, $CO_2\underline{Me}$), 3.35 (s, 3H, $CO_2\underline{Me}$), 3.21 (d, $J_{8\text{-}1}$ = 8.3 Hz, 1H, $H_8$), 2.59 (dddd by decoupling, $J_{1\text{-}7exo}$ = 11.4 Hz, $J_{1\text{-}8}$ = 8.3 Hz, $J_{1\text{-}7endo}$ = 3.7 Hz, $J_{1\text{-}2}$ = 1.6 Hz, 1H, $H_1$), 2.2-2.1 (m, 2H, $H_{2,5}$), 1.65 (s, 15H, $C_5\underline{Me}_5$), 1.7-1.6 (m, obscured by $C_5Me_5$, 1H, $H_6$), 1.13 (d, *J* = 6.9 Hz, 3H, $Me_6$), 1.05-0.8 (m, 2H, $H_{7endo}$, $H_{7exo}$); $^1H$-$^1H$ COSY (400 MHz, $C_6D_6$) δ 3.98 ($H_3$) ↔ δ 3.85 ($H_4$), δ 2.15 ($H_{2,5}$); δ 3.85 ($H_4$) ↔ δ 2.15 ($H_{2,5}$); δ 3.21 ($H_8$) ↔ δ 2.59 ($H_1$); δ 2.59 ($H_1$) ↔ δ 2.15 ($H_{2,5}$), δ 1.0 ($H_{7endo,\ 7exo}$); δ 1.65 ($H_6$)

$\leftrightarrow$ δ 1.13 (Me$_6$); $^{13}$C NMR (75 MHz, C$_6$D$_6$) δ 169.2$^a$ (m, $\underline{C}$O$_2$Me), 168.8$^a$ (m, $\underline{C}$O$_2$Me), 90.1 (s, $\underline{C}_5$Me$_5$), 82.3 (dd, $^1J_{CH}$ = 162.4 Hz, $^2J_{CH}$ = 8.1 Hz, C$_3$), 80.4 (d, $^1J_{CH}$ = 163.0 Hz, C$_4$), 60.1 (d, $^1J_{CH}$ = 132.9 Hz, C$_8$), 59.8 (d, $^1J_{CH}$ = 155 Hz, C$_{2/5}$), 53.5 (d, $^1J_{CH}$ = 140 Hz, C$_{2/5}$), 51.52 (q, $^1J_{CH}$ = 147.1 Hz, CO$_2\underline{Me}$), 51.48 (q, $^1J_{CH}$ = 146.8 Hz, CO$_2\underline{Me}$), 34.4 (t, $^1J_{CH}$ = 127 Hz, C$_7$), 33.6 (d, $^1J_{CH}$ = 130.4 Hz, C$_1$), 31.4 (d, $^1J_{CH}$ = 123.3 Hz, C$_6$), 20.6 (q, $^1J_{CH}$ = 124.9 Hz, Me$_6$), 9.9 (q, $^1J_{CH}$ = 126.1 Hz, C$_5\underline{Me}_5$); $^a$Small unresolved $^2J_{CH}$ and $^3J_{CH}$ complicate the signal. $^1$H-$^{13}$C HETCORR (100 MHz, C$_6$D$_6$) δ 82.3 (C$_3$) $\leftrightarrow$ δ 3.98 (H$_3$); δ 80.4 (C$_4$) $\leftrightarrow$ δ 3.85 (H$_4$); δ 60.1 (C$_8$) $\leftrightarrow$ δ 3.21 (H$_8$); δ 59.8 (C$_{2/5}$) $\leftrightarrow$ δ 2.13 (H$_{2/5}$); δ 53.5 (C$_{2/5}$) $\leftrightarrow$ δ 2.13 (H$_{2/5}$); δ 51.5$^a$ (CO$_2\underline{Me}$) $\leftrightarrow$ δ 3.43 (CO$_2\underline{Me}$), δ 3.35 (CO$_2\underline{Me}$); δ 34.4 (C$_7$) $\leftrightarrow$ δ 1.05-0.9 (H$_{7endo,7exo}$); δ 33.6 (C$_1$) $\leftrightarrow$ δ 2.59 (H$_1$); δ 31.4 (C$_6$) $\leftrightarrow$ δ 1.65 (H$_6$); δ 20.6 (Me$_6$) $\leftrightarrow$ δ 1.13 (Me$_6$); δ 9.9 (C$_5\underline{Me}_5$) $\leftrightarrow$ δ 1.65 (C$_5\underline{Me}_5$). $^a$The signals at δ 51.52 and δ 51.48 are not resolved. MS *m/z* calculated for C$_{23}$H$_{33}$CoO$_4$ (M$^+$): 432.17108; found: 432.17071 (50%).



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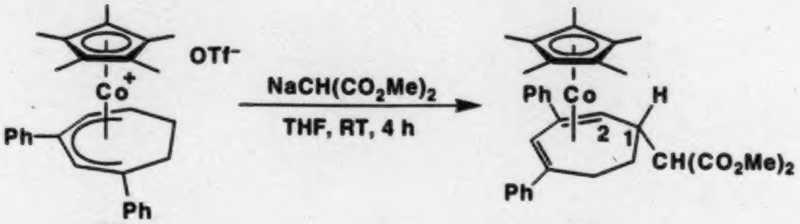
**Pentamethylcyclopentadienyl[dimethyl (2-5-η-5,6-dimethylcyclohepta-2,4-dienyl)malonate]cobalt. [(C$_5$Me$_5$)Co(η$^4$-1-(bis(carbomethoxy)methyl)-5,6-dimethylcyclohepta-2,4-diene)] (196).** In the drybox, a solution of [(C$_5$Me$_5$)Co-η$^5$-5,6-Me$_2$C$_7$H$_7$]$^+$ OTf$^-$ (**102**) (18.2 mg, 0.039 mmol) in tetrahydrofuran (10 mL) was prepared. To this orange solution was added solid sodium dimethylmalonate (27.4 mg, 0.178 mmol, 4.5 equiv) and the solution was stirred for 4 h. A gradual color change to deep red was observed. At the end of 4 h, the solvent was removed *in vacuo* and the residue extracted with pentane until the extracts were colorless. The combined extracts were filtered through a Celite pad and the solvent was removed *in vacuo*, leaving a dark red oil (15.6 mg, 89%). IR (hexane cast, $cm^{-1}$) 2951 (m), 2908 (s), 2855 (m), 1756 (s), 1735 (s), 1434 (s), 1376 (m), 1325 (m), 1306 (m), 1255 (s), 1239 (m), 1223 (m), 1192 (m), 1152 (s), 1027 (m); $^1H$ NMR (400 MHz, $C_6D_6$) δ 4.12 (d, $J_{4\text{-}3}$ = 4.9 Hz, 1H, $H_4$), 3.80 (dd, $J_{3\text{-}4}$ = 4.9 Hz, $J_{3\text{-}2}$ = 7.2 Hz, 1H, $H_3$), 3.38 (s, 3H, $CO_2\underline{Me}$), 3.29 (s, 3H, $CO_2\underline{Me}$), 3.18 (d, $J_{8\text{-}1}$ = 8.3 Hz, 1H, $H_8$), 2.53 (m, dddd by decoupling, $J_{1\text{-}7exo}$ = 12.3 Hz, $J_{1\text{-}8}$ = 8.3 Hz, $J_{1\text{-}7endo}$ = 3.4 Hz, $J_{1\text{-}2}$ < 2 Hz, 1H, $H_1$), 1.96 (br d, $J_{2\text{-}3}$ = 7.1 Hz, 1H, $H_2$), 1.64 (s, 15H, $C_5\underline{Me}_5$), 1.22 (d, $J_{Me\text{-}H6}$ = 6.6 Hz, 3H, $Me_6$), 1.2-1.1 (m, 1H, $H_6$), 1.06 (s, 3H, $Me_5$), 0.90 (m, dddd by decoupling, $J_{7endo\text{-}7exo}$ = 12.3 Hz, $J_{7endo\text{-}1}$ = 3.4 Hz, $J_{7endo\text{-}6}$ = 3.4 Hz, $J_{7endo\text{-}2}$ = small, 1H, $H_{7endo}$), 0.80 (dt, $J_{7exo\text{-}7endo}$ = $J_{7exo\text{-}1}$ = 12 Hz, $J_{7exo\text{-}6}$ = 3.8 Hz, 1H, $H_{7exo}$); $^1H$-$^1H$ COSY (400 MHz, $C_6D_6$) δ 4.12 ($H_4$) ↔ δ 3.80 ($H_3$), δ 1.96 (w, $H_2$); δ 3.80 ($H_3$) ↔ δ 1.96 ($H_2$); δ 3.18 ($H_8$) ↔ δ 2.53 ($H_1$); δ 2.53 ($H_1$) ↔ δ 1.96 ($H_2$), δ 0.90 ($H_{7endo}$), δ 0.80 ($H_{7exo}$); δ 1.96 ($H_2$) ↔ δ 0.90 ($H_{7endo}$); δ 1.22 ($Me_6$) ↔ δ 1.14 ($H_6$); δ 1.14 ($H_6$) ↔ δ 0.90 ($H_{7endo}$), δ 0.80 ($H_{7exo}$); δ 0.90 ($H_{7endo}$) ↔ δ 0.80 ($H_{7exo}$); $^{13}C$ NMR (75 MHz, $C_6D_6$) δ 169.2[a] (m, $\underline{C}O_2Me$), 168.6[a] (m, $\underline{C}O_2Me$), 90.1 (s, $\underline{C}_5Me_5$), 86.7 (d, $^1J_{CH}$ = 159.6 Hz, $C_4$), 78.3 (d, $^1J_{CH}$ = 162.9 Hz, $C_3$), 63.2 (br s, $C_5$), 60.1 (d, $^1J_{CH}$ = 133.4 Hz, $C_8$), 51.8 (d, $^1J_{CH}$ = 147.3 Hz, $C_2$), 51.6[b] (q, $^1J_{CH}$ = 146.8 Hz, $CO_2\underline{Me}$), 51.5[b] (q, $^1J_{CH}$ = 146.8 Hz, $CO_2\underline{Me}$), 38.2 (d, $^1J_{CH}$ = 120.9 Hz, $C_6$), 34.7 (t, $^1J_{CH}$ = 127.8 Hz, $C_7$), 33.5 (d, $^1J_{CH}$ = 134.4 Hz, $C_1$), 27.7 (qt, $^1J_{CH}$ = 124.4 Hz, $^3J_{CH}$ = 4.1 Hz, $Me_5$), 19.4 (q, $^1J_{CH}$ = 124.9 Hz, $Me_6$), 9.9 (q, $^1J_{CH}$ = 126.1 Hz, $C_5\underline{Me}_5$). [a]Small unresolved $^2J_{CH}$ and $^3J_{CH}$ complicate the signal. [b]These signals overlap in gated spectrum. $^1H$-$^{13}C$ HETCORR (100 MHz, $C_6D_6$) δ 86.7 ($C_4$) ↔ δ 4.12 ($H_4$); δ 78.3 ($C_3$) ↔ δ 3.80 ($H_3$); δ 60.1 ($C_8$) ↔ δ 3.18 ($H_8$); δ 51.8 ($C_2$) ↔ δ 1.96 ($H_2$); δ 51.6 ($CO_2\underline{Me}$) ↔ δ 3.38 ($CO_2\underline{Me}$), δ 3.29 ($CO_2\underline{Me}$); δ 38.2 ($C_6$) ↔ δ 1.14 ($H_6$); δ 34.7 ($C_2$) ↔ δ 0.90 ($H_{7endo}$), δ 0.80 ($H_{7exo}$); δ 33.5 ($C_1$) ↔ δ 2.53 ($H_1$); δ 27.7 ($Me_5$) ↔ δ 1.06 ($Me_5$); δ 19.4 ($Me_6$) ↔ δ 1.22 ($Me_6$); δ 9.9 ($C_5\underline{Me}_5$) ↔ δ 1.64 ($C_5\underline{Me}_5$); MS *m/z* calculated for $C_{24}H_{35}CoO_4$ ($M^+$): 446.18674; found: 446.18715 (58%).



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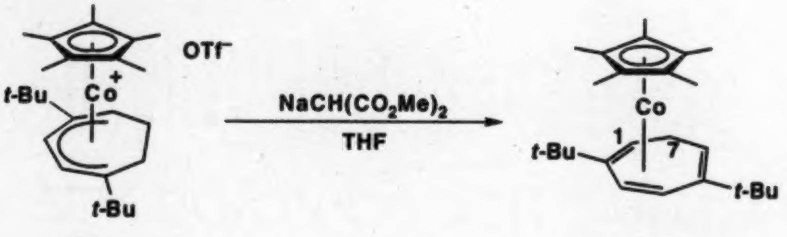
**Pentamethylcyclopentadienyl[dimethyl (2-5-η-3,5-diphenylcyclohepta-2,4-dienyl)malonate]cobalt. [($C_5Me_5$)Co($\eta^4$-1-(bis(carbomethoxy)methyl)-3,5-diohenylcyclohepta-2,4-diene)] (197).** In the drybox, a solution of [($C_5Me_5$)Co-$\eta^5$-3,5-$Ph_2$-$C_7H_7$]$^+$ OTf$^-$ (**95**) (43.9 mg, 0.075 mmol) in tetrahydrofuran (10 mL) was prepared. To this dark red solution, solid sodium dimethylmalonate (40.0 mg, 0.259 mmol, 3.5 equiv) was added and the solution was stirred for 4 h. A slight darkening in color was observed. At the end of 4 h, the solvent was removed *in vacuo* and the residue extracted with pentane until the extracts were colorless. The combined extracts were filtered through a Celite pad and the solvent was removed *in vacuo*, leaving a dark red oily solid (30.6 mg, 72%). IR (hexane cast, cm$^{-1}$) 2953 (m), 2916 (m), 1767 (s), 1734 (s), 1449 (m), 1434 (m), 1261 (s), 1236 (m), 1194 (m), 1153 (m), 1127 (m), 1068 (m), 1024 (s), 799 (m), 696 (m); $^1$H NMR (400 MHz, $C_6D_6$) δ 7.93 (d, $J$ = 7.2 Hz, 2H, $H_{Ph}$), 7.48 (d, $J$ = 7.6 Hz, 2H, $H_{Ph}$), 7.34 (t, $J$ = 7.6 Hz, 2H, $H_{Ph}$), 7.28 (t, $J$ = 7.3 Hz, 2H, $H_{Ph}$), 7.26 (t, $J$ = 7.6 Hz, 2H, $H_{Ph}$), 7.13 (t, $J$ = 7.3 Hz, 2H, $H_{Ph}$), 5.93 (s, 1H, $H_4$), 3.60 (d, $J_{1\text{-}8}$ = 9.9 Hz, 1H, $H_8$), 3.50 (s, 3H, $CO_2\underline{Me}$), 3.35 (s, 3H, $CO_2\underline{Me}$), 2.71 (br t, $J_{obs}$ = 11 Hz, 1H, $H_1$), 2.66 (br s, 1H, $H_2$), 1.85 (ddd, $J_{6endo\text{-}6exo}$ = 16 Hz, $J_{6endo\text{-}7exo}$ = 12.4, $J_{6endo\text{-}7endo}$ = 3.0, 1H, $H_{6endo}$), 1.70 (ddd, $J_{6exo\text{-}6endo}$ = 16 Hz, $J_{6exo\text{-}7exo}$ = 2.9 Hz, $J_{6exo\text{-}7endo}$ = 3.4 Hz, 1H, $H_{6exo}$), 1.55 (br d, $J_{obs}$ = 14 Hz, 1H, $H_{7endo}$), 1.21 (s, 15H, $C_5\underline{Me_5}$), 0.67 (qd, $J_{7exo\text{-}7endo}$ = $J_{7exo\text{-}1}$ = $J_{7exo\text{-}6endo}$ = 12.4 Hz, $J_{7exo\text{-}6exo}$ = 2.9 Hz, 1H, $H_{7exo}$); $^1$H-$^1$H COSY (400 MHz, $C_6D_6$) δ 5.93 ($H_4$) ↔ δ 2.66 (w, $H_2$), 1.70 (w, $H_{6exo}$); δ 3.60 ($H_8$) ↔ δ 2.71 ($H_1$); δ 2.71 ($H_1$) ↔ δ 2.66 ($H_2$), δ 1.55 ($H_{7endo}$), 0.69 ($H_{7exo}$); δ 2.66 ($H_2$) ↔ δ 1.55

($H_{7endo}$); δ 1.85 ($H_{6endo}$) ↔ δ 1.70 ($H_{6exo}$), 0.69 ($H_{7exo}$); δ 1.70 ($H_{6exo}$) ↔ δ 0.69 ($H_{7exo}$); δ 1.55 ($H_{7endo}$) ↔ δ 0.69 ($H_{7exo}$); $^{13}C$ NMR (75 MHz, $C_6D_6$) δ 169.4$^a$ (m, $\underline{C}O_2Me$), 168.3$^a$ (m, $\underline{C}O_2Me$), 150.4 (s, $C_{ipso}$), 142.3 (s, $C_{ipso}$), 128.1$^b$ ($C_{Ph}$), 127.0$^b$ ($C_{Ph}$), 125.2 (dt, $^1J_{CH}$ = 157.7 Hz, $^2J_{CH}$ = 7 Hz, $C_{Ph}$), 123.7 (dt, $^1J_{CH}$ = 160.2 Hz, $^2J_{CH}$ = 7 Hz, $C_{Ph}$), 90.7 (s, $\underline{C}_5Me_5$), 88.3 (s, $C_3$), 81.0 (d, $^1J_{CH}$ = 159.3 Hz, $C_4$), 60.4 (d, $^1J_{CH}$ = 134.7 Hz, $C_8$), 53.6 (s, $C_5$), 51.8 (q, $^1J_{CH}$ = 147.0 Hz, $CO_2\underline{Me}$), 51.7 (q, $^1J_{CH}$ = 147.1 Hz, $CO_2\underline{Me}$), 47.2 (d, $^1J_{CH}$ = 151.6 Hz, $C_2$), 39.0 (d, $^1J_{CH}$ = 130.4 Hz, $C_1$), 33.8 (t, $^1J_{CH}$ = 127 Hz, $C_6$), 27.8 (t, $^1J_{CH}$ = 127 Hz, $C_7$), 8.4 (q, $^1J_{CH}$ = 126.2 Hz, $C_5\underline{Me_5}$). $^a$Small unresolved $^2J_{CH}$ and $^3J_{CH}$ complicate the signal. $^b$Phenyl C's obscured by solvent in gated decoupled spectrum. $^1H$-$^{13}C$ HETCORR (100 MHz, $C_6D_6$) δ 81.0 ($C_4$) ↔ δ 5.93 ($H_4$); δ 60.4 ($C_8$) ↔ δ 3.60 ($H_8$); δ 51.8/51.7$^a$ ($CO_2\underline{Me}$) ↔ δ 3.50, 3.35 ($CO_2\underline{Me}$); δ 47.2 ($C_2$) ↔ δ 2.66 ($H_2$); δ 39.0 ($C_1$) ↔ δ 2.71 ($H_1$); δ 33.8 ($C_6$) ↔ δ 1.85 ($H_{6endo}$), δ 1.70 ($H_{6exo}$); δ 27.8 ($C_7$) ↔ δ 1.55 ($H_{7endo}$), δ 0.69 ($H_{7exo}$); δ 8.4 ($C_5\underline{Me_5}$) ↔ δ 1.21 ($C_5\underline{Me_5}$). $^a$Signals are not resolved. MS *m/z* calculated for $C_{34}H_{39}CoO_4$ ($M^+$): 570.21802; found: 570.21688 (44%).



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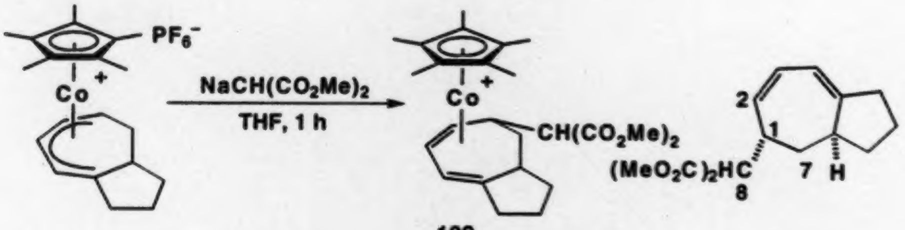
**($C_5Me_5$)Co(1-4-η-2,5-di-*t*-butyl-1,3,5-cycloheptatriene) (198).** In the drybox, a vial was charged with ($\eta^5$-$C_5Me_5$)Co($\eta^5$-1,4-*t*-$Bu_2$-$C_7H_7$)]$^+$ $OTf^-$ (**96**) (18.3 mg, 33.4 μmol) and sodium dimethylmalonate (7.0 mg, 45.5 μmol, 1.4 equiv). Precooled (-35°C) THF (about 4 mL) was added and the solution was allowed to warm to room temperature. The solution was stirred for 5 h and all volatile material was removed *in vacuo*. The red residue (about 8 mg, 60%) was examined directly by $^1H$ NMR spectroscopy. $^1H$ NMR

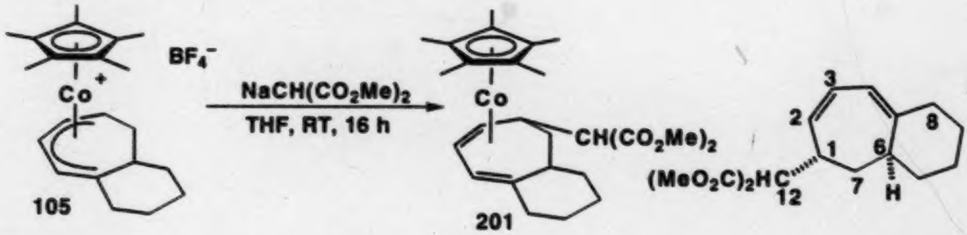
(400 MHz, $C_6D_6$) δ 5.19 (br s, 1H, $H_6$), 4.45 (d, *J* = 7.1 Hz, 1H, $H_3$), 2.57 (br s, 1H, $H_1$), 2.47 (d, *J* = 7.1 Hz, 1H, $H_4$), 2.20 (dt, *J* ca. 17, 3 Hz, 1H, $H_{7a}$), 1.81 (s, 15H, $C_5\underline{Me}_5$), 1.27 (m, 1H, $H_{7b}$, obscured by *t*-Bu groups) 1.26 (s, 9H, *t*-Bu), 1.24 (s, 9H, *t*-Bu); $^1H$-$^1H$ COSY (400 MHz, $C_6D_6$) δ 5.19 ($H_6$) ↔ δ 2.46 (w, $H_4$), 2.20 ($H_{7a}$), 1.27 ($H_{7b}$); δ 4.45 ($H_3$) ↔ δ 2.46 ($H_4$); δ 2.57 ($H_1$) ↔ δ 2.20 ($H_{7a}$), 1.27 ($H_{7b}$); δ 2.20 ($H_{7a}$) ↔ δ 1.27 ($H_{7b}$); $^{13}C$ NMR (100 MHz, APT, $C_6D_6$) δ 147.5 ($C_2$), 114.3 ($C_1$), 107.9 ($C_5$), 89.4 ($\underline{C}_5Me_5$), 81.1 ($C_4$), 47.9 ($C_{3/6}$), 44.8 ($C_{3/6}$), 36.0 ($\underline{C}Me_3$), 34.5 ($\underline{C}Me_3$), 30.7 (*t*-Bu), 30.4 (*t*-Bu), 30.3 ($C_7$), 10.7 ($C_5\underline{Me}_5$). MS *m/z* calculated for $C_{25}H_{39}Co$ ($M^+$): 398.23837; found: 398.23808 (42%). MS *m/z* calculated for $C_{21}H_{30}Co$ ($M^+$- *t*-Bu): 341.16794; found: 341.16803 (100%).



111

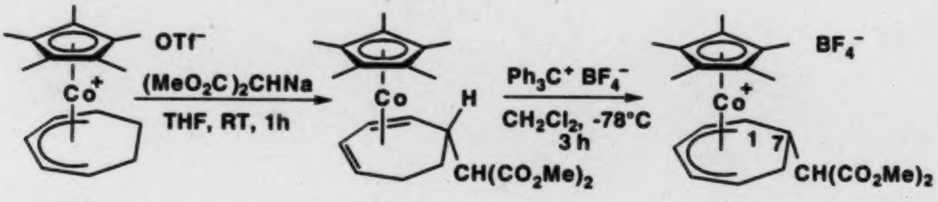
199

**($C_5Me_5$)[dimethyl (1-4η–bicyclo[5.3.0]deca-1,3-dien-5-yl)malonate]cobalt. [($C_5Me_5$)Co($\eta^4$-5-(bis(carbomethoxy)methyl)bicyclo[5.3.0]deca-1,3-diene)] (199).** To a suspension of [($C_5Me_5$)Co($\eta^5C_{10}H_{13}$)]$^+$ $PF_6^-$ (**111**) (83.6 mg, 0.177 mmol) in tetrahydrofuran (10 mL) was added sodium dimethylmalonate (59.6 mg, 0.387 mmol, 2.2 equiv). The mixture was stirred for 1h at ambient temperature. All volatile material was then removed *in vacuo* and the residue was extracted with pentane until the extracts were colorless. The combined extracts were filtered through a Celite pad and the solvent was removed, leaving a red oil (35.6 mg, 44%). IR (hexane cast, $cm^{-1}$) 2946 (s), 2910 (s), 2857 (s), 1758 (s), 1736 (s), 1433 (m), 1381 (m), 1295 (m), 1260 (m), 1207 (m), 1140 (s), 1027 (m); $^1H$ NMR (400 MHz, $C_6D_6$) δ 4.54 (d, $J_{4\text{-}3}$ = 4.8 Hz, 1H, $H_4$), 3.86 (dd, $J_{3\text{-}4}$ = 4.5 Hz, $J_{3\text{-}2}$ = 7.8 Hz, 1H, $H_3$), 3.39 (s, 3H, $CO_2\underline{Me}$), 3.24 (s, 3H, $CO_2\underline{Me}$), 3.2-3.1 (m, 1H, $H_1$), 3.09 (d, $J_{8\text{-}1}$ = 11.4 Hz, 1H, $H_8$), 2.58 (br t, $J_{2\text{-}3} = J_{2\text{-}1}$ = 7.5 Hz, 1H, $H_2$), 1.79 (ddd, $J$ = 11.5, 11.5, 5.8 Hz, 1H, $CH_2$), 1.7-1.4 (series of m, $CH_2$, $H_{7endo}$), 1.59 (s, 15H, $C_5Me_5$), 1.16 (ddd, $J_{7exo\text{-}7endo} = J_{7exo\text{-}1}$ = 12 Hz, $J_{7exo\text{-}6}$ = 4.2 Hz, 1H, $H_{7exo}$), 0.72-0.60 (m, 1H, $H_{6exo}$); $^1H\text{-}^1H$ GCOSY (300 MHz, $C_6D_6$) δ 4.54 ($H_4$) ↔ δ 3.86 ($H_3$), δ 2.58 (w, $H_2$); δ 3.86 ($H_3$) ↔ δ 2.58 ($H_2$); δ 3.15 ($H_1$) ↔ δ 3.09 ($H_8$), δ 2.58 ($H_2$), δ 1.70 ($H_{7endo}$), δ 1.16 ($H_{7exo}$); δ 1.79 ($CH_2$) ↔ δ 1.16 ($H_{7exo}$), δ 0.66 ($H_6$); δ 1.70 ($H_{7endo}$) ↔ δ 1.16 ($H_{7exo}$), δ 0.66 ($H_6$); δ 1.16 ($H_{7exo}$) ↔ δ 0.66 ($H_6$); $^{13}C$ NMR (100 MHz, $C_6D_6$) δ 169.4 (s, $CO_2Me$), 169.0 (s, $CO_2Me$), 89.6 (s, $C_5Me_5$), 87.1 (d, $^1J_{CH}$ = 163.6 Hz, $C_4$), 79.0 (d, $^1J_{CH}$ = 162.2 Hz, $C_3$), 73.7 (s, $C_5$), 57.7 (d, $^1J_{CH}$ = 135.1 Hz, $C_2$), 55.9 (d, $^1J_{CH}$ = 136.7 Hz, $C_1$), 51.64$^a$ (q, $^1J_{CH}$ = 146.8 Hz, $CO_2\underline{Me}$), 51.55$^a$ (q, $^1J_{CH}$ = 147.1 Hz, $CO_2\underline{Me}$), 40.1$^b$ (t, $^1J_{CH}$ = 131.3 Hz, $CH_2$), 39.3$^b$ (t, $^1J_{CH}$ = 124.4 Hz, $C_7$), 38.4$^b$ (d, $C_6$), 37.2$^a$ (t, $CH_2$), 35.9 (d, $^1J_{CH}$ = 130.7 Hz, $C_8$), 27.1 (t, $^1J_{CH}$ = 130.1 Hz, $CH_2$), 9.8 (q, $^1J_{CH}$ = 126.3 Hz, $C_5\underline{Me_5}$). $^{a,b}$Signals are not resolved in the gated decoupled spectrum. HMQC (300 MHz, $C_6D_6$) δ 87.1 ($C_4$) ↔ δ 4.54 ($H_4$); δ 79.0 ($C_3$) ↔ δ 3.86 ($H_3$); δ 57.7 ($C_2$) ↔ δ 2.58 ($H_2$); δ 55.9 ($C_1$) ↔ δ 3.15 ($H_1$); δ 51.64/51.55 ($CO_2\underline{Me}$) ↔ δ 3.29 ($CO_2Me$), δ 3.24 ($CO_2Me$); δ 40.1 ($CH_2$) ↔ δ 1.79 ($CH_2$), δ 1.50 ($CH_2$); δ 39.3 ($C_7$) ↔ δ 1.70 ($H_{7endo}$), δ 1.16 ($H_{7exo}$); δ 38.4 ($C_6$) ↔ δ 0.66 ($H_6$); δ 37.2 ($CH_2$) ↔ δ 1.80 ($CH_2$); δ 35.9 ($C_8$) ↔ δ 3.09 ($H_8$); δ 27.1 ($CH_2$) ↔ δ 1.75 ($CH_2$), δ 1.4 ($CH_2$); δ 9.8 ($C_5\underline{Me_5}$) ↔ δ 1.59 ($C_5\underline{Me_5}$). MS *m/z* calculated for $C_{25}H_{35}CoO_4$ ($M^+$): 458.18674; found: 458.18623 (29%). MS *m/z* calculated for $C_{20}H_{27}Co$ ($M^+$ - dimethylmalonate): 326.14447; found: 326.14402 (100%).



**$(C_5Me_5)$[dimethyl (1-4η–bicyclo[5.4.0]undeca-1,3-dien-5-yl)malonate]cobalt. [$(C_5Me_5)Co(\eta^4$-5-(bis(carbomethoxy)methyl)bicyclo[5.4.0]undeca-1,3-diene)] (201).** In the drybox, $[(C_5Me_5)Co\text{-}\eta^5\text{-}C_{11}H_{15}]^+ BF_4^-$ (**105**) (102.9 mg, 0.2403 mmol) was placed in a 50 mL Schlenk flask. Tetrahydrofuran (20 mL) was added to form an orange-red slurry and sodium dimethylmalonate (51.7 mg, 1.4 equiv) was added. The slurry slowly dissolved and the solution turned deep red. The reaction was stirred overnight, then all volatiles were removed *in vacuo*. The residue was extracted with pentane and the pentane extracts were combined and filtered through a pad of Celite. The solvent was removed, leaving 108.8 mg (96%) of a deep red oil. IR (hexane cast, $cm^{-1}$) 2948 (m), 2912 (s), 2852 (m), 2807 (w), 1757 (s), 1735 (s), 1434 (m), 1380 (w), 1327 (w), 1283 (w), 1257 (m), 1240 (m), 1190 (w), 1171 (m), 1151 (s), 1101 (w), 1027 (m); $^1H$ NMR (400 MHz, $C_6D_6$) δ 4.18 (d, $J_{4\text{-}3}$ = 4.9 Hz, 1H, $H_4$), 3.58 (dd, $J_{3\text{-}4}$ = 4.9 Hz, $J_{3\text{-}2}$ = 7.3 Hz, 1H, $H_3$), 3.44 (s, 3H, $CO_2\underline{Me}$), 3.36 (s, 3H, $CO_2\underline{Me}$), 3.30 (d, $J_{12\text{-}1}$ = 8.5 Hz, 1H, $H_{12}$), 2.58 (dddd by decoupling, $J_{1\text{-}7exo}$ = 11.6 Hz, $J_{1\text{-}12}$ = 8.3 Hz, $J_{1\text{-}7endo}$ = 3.6 Hz, $J_{1\text{-}2}$ = 1.3 Hz, 1H, $H_1$), 2.18 (br d, $J_{2\text{-}3}$ = 7.2 Hz, 1H, $H_2$), 2.0-1.6 (series of m, 4H, $CH_2$, $H_7$), 1.73 (s, 15H, $C_5\underline{Me_5}$), 1.6-1.4 (series of m, 4H, $CH_2$), 1.2-0.9 (series of m, 3H, $CH_2$, $H_6$); $^1H$-$^1H$ GCOSY (300 MHz, $C_6D_6$) δ 4.18 ($H_4$) ↔ δ 3.58 ($H_3$); δ 3.58 ($H_3$) ↔ δ 2.18 ($H_2$); δ 3.30 ($H_{12}$) ↔ δ 2.58 ($H_1$); δ 2.58 ($H_1$) ↔ δ 2.18 (w, $H_2$), δ 1.1 ($H_7$), 1.2 (w, $H_7$); δ 2.18 ($H_2$) ↔ δ 1.2 ($H_7$); $^{13}C$ NMR (100 MHz, $C_6D_6$) δ $169.1^a$ (m, $\underline{C}O_2Me$), $168.6^a$ (m, $\underline{C}O_2Me$), 90.1 (s, $\underline{C_5}Me_5$), 84.8 (d, $^1J_{CH}$ = 157.1 Hz, $C_4$), 78.2 (d, $^1J_{CH}$ = 160.8 Hz, $C_3$), 65.4 (s, $C_5$), 60.2 (d, $^1J_{CH}$ = 133.1 Hz, $C_{12}$), $53.0^b$ (d, $^1J_{CH}$ = 146.9 Hz, $C_2$), $51.5^b$ (q, $^1J_{CH}$ = 149.6 Hz, $CO_2\underline{Me}$), 42.5 (d, $^1J_{CH}$ = 121.1 Hz, $C_6$), 38.5 (t, $^1J_{CH}$ = 123.2 Hz, $CH_2$), $35.6^c$ (t, $^1J_{CH}$ = 124 Hz, $CH_2$), $35.0^c$ (d, $^1J_{CH}$ = 128.8 Hz, $C_1$), $32.7^c$ (t, $^1J_{CH}$ = 126.4 Hz, $CH_2$), $27.9^d$ (t, $^1J_{CH}$ = 126.3 Hz, $CH_2$), $26.6^d$ (t, $^1J_{CH}$ = 125.2 Hz, $C_7$), 10.0 (q, $^1J_{CH}$ = 126.1 Hz, $C_5\underline{Me_5}$). $^a$Signal is complicated by the presence of $^{2,3}J_{CH}$. $^{b,c,d}$Denote pairs of overlapping signals in the gated spectrum: $J_{CH}$'s are approximate. The $C_1$ assignment is based on $^{13}C$ multiplicity (doublet). HMQC (300 MHz, $C_6D_6$) δ 84.8 ($C_4$)

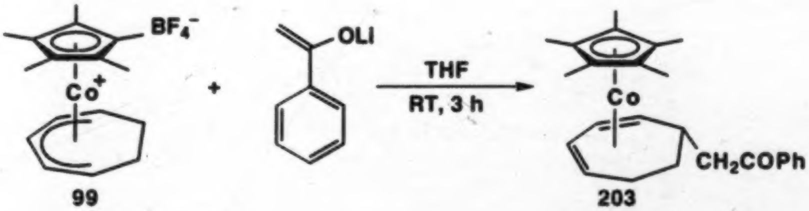
↔ $\delta$ 4.18 ($H_4$); $\delta$ 78.2 ($C_3$) ↔ $\delta$ 3.58 ($H_3$); $\delta$ 60.2 ($C_{12}$) ↔ $\delta$ 3.30 ($H_{12}$); $\delta$ 53.0 ($C_2$) ↔ $\delta$ 2.18 ($H_2$); $\delta$ 51.5 ($CO_2\underline{Me}$) ↔ $\delta$ 3.34 ($CO_2\underline{Me}$), $\delta$ 3.36 ($CO_2\underline{Me}$); $\delta$ 42.5 ($C_6$) ↔ $\delta$ 0.9 ($H_6$); $\delta$ 38.5 ($CH_2$) ↔ $\delta$ 1.5 ($CH_2$); $\delta$ 35.6 ($CH_2$) ↔ $\delta$ 1.1 ($CH_2$); $\delta$ 35.0 ($C_1$) ↔ $\delta$ 2.58 ($H_1$); $\delta$ 32.7 ($CH_2$) ↔ $\delta$ 1.5 ($CH_2$); $\delta$ 27.9 ($CH_2$) ↔ $\delta$ 1.8 ($CH_2$); $\delta$ 26.6 ($C_7$) ↔ $\delta$ 1.7 ($H_7$); $\delta$ 10.0 ($C_5\underline{Me_5}$) ↔ $\delta$ 1.7 ($C_5\underline{Me_5}$). HMQC correlations for high field signals are based on chemical shift value, rather than to a specific signal. MS *m/z* calculated for $C_{26}H_{37}CoO_4$ ($M^+$): 472.20239; found: 472.20331 (0.50%).



**99** **192** **202**

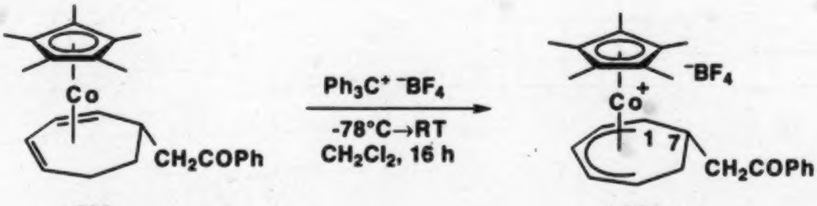
**[($C_5Me_5$)Co($\eta^5$-7-(bis(carbomethoxy)methyl)-$C_7H_8$)]$^+$ $BF_4^-$ (202).** In the drybox, ($C_5Me_5$)Co($\eta^5$-$C_7H_9$)(OTf) (**99**) (102.7 mg, 0.2353 mmol) was dissolved in tetrahydrofuran (20 mL) at room temperature. Sodium dimethylmalonate (43.5 mg, 1.2 equiv) was added with stirring and the solution was stirred for 1 h before the solvent was removed *in vacuo*. The residue was extracted into pentane and the solution filtered through a Celite pad. The pentane was removed, leaving of a red oil (85.5 mg, 87%). The crude product (**192**) was mixed with triphenylmethyl (trityl) tetrafluoroborate (87.6 mg, 2.65 mmol, 1.3 equiv) and immediately taken outside the drybox and cooled to -78 °C. Freshly distilled dichloromethane (5 mL) was added to the flask and the cooling bath removed. The solution was stirred 3 h at room temperature. After removing the solvent and washing with diethyl ether, the residue was flash chromatographed (silica gel, 5% methanol/dichloromethane), leaving a light orange solid (61.7 mg, 60% from diene, 52% overall). IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3067 (w), 2957 (w), 2922 (w), 1730 (s), 1455 (m), 1436 (m), 1389 (m), 1357 (w), 1331 (m), 1287 (m), 1264 (m), 1242 (m), 1215 (m), 1195 (m), 1055 (s), 1036 (s), 980 (w), 957 (w), 918 (w), 893 (w), 874 (w), 847 (w), 732 (w), 700 (w), 520 (w), 510 (w), 494 (w); $^1$H

NMR (400 MHz, $CDCl_3$) δ 6.71 (apparent t, $J_{3\text{-}2}$ = 6.9 Hz, $J_{3\text{-}4}$ = 5.9 Hz, 1H, $H_3$), 5.47 (apparent t, $J_{4\text{-}3}$ = 5.4 Hz, $J_{4\text{-}5}$ = 7.7 Hz, 1H, $H_4$), 4.89 (dd, $J_{2\text{-}1}$ = 9.3 Hz, $J_{2\text{-}3}$ = 7.0 Hz, 1H, $H_2$), 4.40 (br d, $J_{1\text{-}2}$ = 8.3 Hz, 1H, $H_1$), 4.23 (br q, $J_{5\text{-}4}$ = $J_{5\text{-}3}$ = 8 Hz, $J_{5\text{-}6exo}$ = 4.8 Hz, $J_{5\text{-}3}$ < 1 Hz, 1H, $H_5$), 3.72 (s, 3H, OMe), 3.67 (s, 3H, OMe), 3.62 (m, overlaps with δ 3.67, 1H, $H_{7endo}$), 3.07 (d, $J_{8\text{-}7endo}$ = 7.7 Hz, 1H, $H_8$), 1.89 (s, 15H, $C_5Me_5$), 1.88 (m, 1H, $H_{6endo}$ obscured by $C_5\underline{Me_5}$), 0.14 (ddd $J_{6exo\text{-}6endo}$ = $J_{6exo\text{-}7endo}$ = 12.1 Hz, $J_{6exo\text{-}5}$ = 4.8 Hz, 1H, $H_{6exo}$); $^1H$-$^1H$ GCOSY (300 MHz, $CD_2Cl_2$) δ 6.71 ($H_3$) ↔ δ 5.47 ($H_4$), δ 4.89 ($H_2$), δ 4.23 (w, $H_5$); δ 5.47 ($H_4$) ↔ δ 4.23 ($H_5$); δ 4.89 ($H_2$) ↔ δ 4.40 ($H_1$); δ 4.40 ($H_1$) ↔ δ 3.62 (w, $H_{7endo}$), δ 1.89 (w, $H_{6endo}$); δ 4.23 ($H_5$) ↔ δ 1.89 ($H_{6endo}$), δ 0.14 ($H_{6exo}$); δ 3.62 ($H_{7endo}$) ↔ δ 3.07 ($H_8$), δ 1.89 (w, $H_{6endo}$), δ 0.14 (w, $H_{6exo}$); δ 1.89 ($H_{6endo}$) ↔ δ 0.14 ($H_{6exo}$); $^{13}C$ NMR (75 MHz, $CD_2Cl_2$) δ 167.9 (s, $\underline{C}O_2Me$), 101.2 (d, $^1J_{CH}$ = 174.5 Hz, $C_3$), 99.8 (d, $^1J_{CH}$ = 175.6 Hz, $C_4$), 97.6 (d, $^1J_{CH}$ = 167.3 Hz, $C_2$), 89.6 (d, $^1J_{CH}$ = 150.0 Hz, $C_5$), 84.7 (d, $^1J_{CH}$ = 159.0 Hz, $C_1$), 56.2 (d, $^1J_{CH}$ = 132.3 Hz, $C_8$), 53.0 (q, $^1J_{CH}$ = 148.8 Hz, $CO_2\underline{Me}$), 52.2 (d, $^1J_{CH}$ = 135 Hz, partially obscured by solvent, $C_7$), 29.1 (t, $^1J_{CH}$ = 132.2 Hz, $C_6$), 9.8 (q, $^1J_{CH}$ = 129.0 Hz, $C_5\underline{Me_5}$); HMQC (300 MHz, $CD_2Cl_2$) δ 101.2 ($C_3$) ↔ δ 6.71 ($H_3$); δ 99.8 ($C_4$) ↔ δ 5.47 ($H_4$); δ 97.6 ($C_2$) ↔ δ 4.89 ($H_2$); δ 89.6 ($C_5$) ↔ δ 4.40 ($H_5$); δ 84.7 ($C_1$) ↔ δ 4.23 ($H_1$); δ 56.2 ($C_8$) ↔ δ 3.07 ($H_8$); δ 53.0/52.2 ($CO_2\underline{Me}$, $C_7$) ↔ δ 3.72/3.67 ($CO_2\underline{Me}$), δ 3.62 ($H_7$); δ 29.1 ($C_6$) ↔ δ 1.88 ($H_{6endo}$), δ 0.14 ($H_{6exo}$); δ 9.8 ($C_5\underline{Me_5}$) ↔ δ 1.89 ($C_5\underline{Me_5}$). Analysis calculated for $C_{22}H_{30}CoBF_4O_4$: C, 52.41; H, 6.00; found: C, 52.249; H, 6.209.



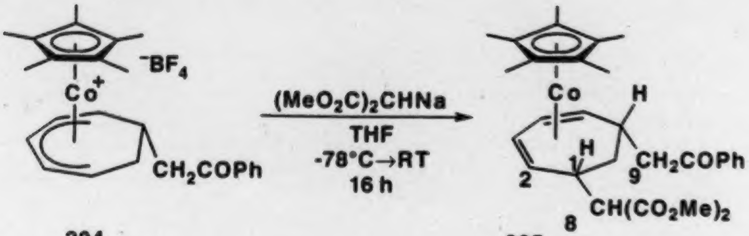
**Pentamethylcyclopentadienyl[1-(2-5η–cyclohepta-2,4-dienyl)acetophenone] cobalt (203).** In the drybox, a Schlenk flask was charged with $[(C_5Me_5)Co(C_7H_9)]^+ BF_4^-$ **(99)**

(0.1290 mg, 0.2956 mmol) and tetrahydrofuran (6 mL) was added to form an orange slurry. The lithium enolate of acetophenone (1.5 equiv, 55.9 mg) was added as a solid powder and the reaction mixture was stirred 3 h. All volatile material was removed *in vacuo* and the residue was extracted with pentane until the extracts were colorless. The pentane solution was filtered through a Celite pad and the pentane was removed. An orange oil (74.1 mg, 62%) remained. The crude compound was used in further reactions without full characterization. IR (hexane cast, $cm^{-1}$) 3059 (m), 2959 (s), 2909 (s), 2861 (s), 1679 (s), 1652 (w), 1598 (m), 1580 (w), 1494 (w), 1447 (s), 1380 (m), 1349 (m), 1331 (m), 1261 (s), 1222 (m), 1176 (m), 1029 (s), 800 (s), 764 (m), 750 (m), 699 (s), 667 (w), 639 (w), 589 (w), 506 (w). $^1H$ NMR (400 MHz, $C_6D_6$, select data) δ 7.92 (m, $H_{Ph}$), 7.08 (m, $H_{Ph}$), 4.1-3.9 (m, 2H, $H_{3,4}$), 2.74 (d, *J* = 7.3 Hz, 2H, $CH_2$), 2.4-1.4 (series of m), 1.48 (s, 15H, $C_5\underline{Me_5}$); MS *m/z* calculated for $C_{25}H_{31}CoO$ ($M^+$): 406.17068; found: 406.17093 (100%).



**203** **204**

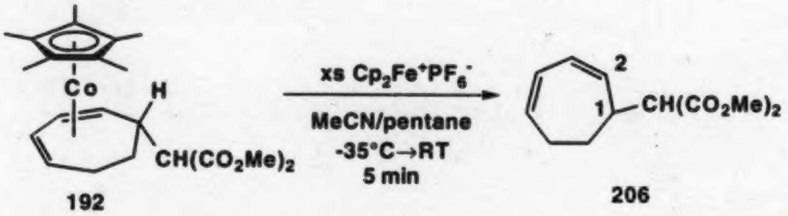
**Pentamethylcyclopentadienyl[1-(2-6η–cyclohepta-2,4-dien-6-yl)acetophenone] cobalt. [($C_5Me_5$)Co($\eta^5$-6-(acetophenone)-$C_7H_8$)]$^+$ $BF_4^-$ (204).** Note that the numbering given below is for convenience of tabulation of NMR spectroscopic data and is not the same as that used for naming the complex. In the drybox, a Schlenk flask was charged with ($\eta^5$-$C_5Me_5$)Co($\eta^4$-1-($C_8H_7O$)-$C_7H_8$) **(203)** (85.8 mg, 0.211 mmol) and removed to the Schlenk line. Dichloromethane (10 mL) was added and the flask was cooled to -78°C. Trityl tetrafluoroborate (119.3 mg, 1.7 equiv) was added and the reaction was allowed to warm slowly overnight to room temperature. The solvent volume was reduced to about 3 mL and the product precipitated by the addition of wet diethyl ether. The product was purified by flash chromatography on silica gel, eluting with 5% methanol/dichloromethane, yielding a light orange powder (30.7 mg, 30%). IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3075 (vw), 2975 (vw), 2917 (w), 1680 (m), 1596 (w), 1580 (w), 1449 (w), 1384 (w), 1358 (w), 1274 (w), 1182 (w), 1055 (s), 908 (w), 757 (w), 732 (w), 694 (w), 520 (w); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.86 (d, $J$ = 7.7 Hz, 2H, $H_{Ph}$), 7.54 (t, $J$ = 7.2 Hz, $H_{Ph}$), 7.43 (t, $J$ = 7.5 Hz, 2H, $H_{Ph}$), 6.69 (t, $J$ = 6.2 Hz, 1H, $H_3$), 5.42 (t, $J$ = 6.8 Hz, 1H, $H_4$), 4.86 (dd, $J$ = 9.1, 7.2 Hz, 1H, $H_2$), 4.54 (br d, $J$ = 8.1 Hz, 1H, $H_1$), 4.27-4.18 (m, 1H, $H_5$), 3.65-3.55 (m, 1H, $H_{7endo}$), 2.93 (dd, $J$ = 17.7, 6.7 Hz, 1H, $H_{8a}$), 2.77 (dd, $J$ = 17.5, 6.8 Hz, 1H, $H_{8b}$), 2.1-2.0 (m, 1H, $H_{6endo}$), 1.90 (s, 15H, $C_5\underline{Me}_5$), 0.04 (ddd, $J$ = 10.1, 10.1, 4.9 Hz, 1H, $H_{6exo}$); $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) $\delta$ 7.86 ($H_{Ph}$) $\leftrightarrow$ $\delta$ 7.43 ($H_{Ph}$); $\delta$ 7.54 ($H_{Ph}$) $\leftrightarrow$ $\delta$ 7.43 ($H_{Ph}$); $\delta$ 6.69 ($H_3$) $\leftrightarrow$ $\delta$ 5.42 ($H_4$), $\delta$ 4.86 ($H_2$); $\delta$ 5.42 ($H_4$) $\leftrightarrow$ $\delta$ 4.23 ($H_5$); $\delta$ 4.86 ($H_2$) $\leftrightarrow$ $\delta$ 4.54 ($H_1$); $\delta$ 4.54 ($H_1$) $\leftrightarrow$ $\delta$ 3.60 ($H_{7endo}$); $\delta$ 4.23 ($H_5$) $\leftrightarrow$ $\delta$ 2.05 ($H_{6endo}$), $\delta$ 0.04 ($H_{6exo}$); $\delta$ 3.60 ($H_{7endo}$) $\leftrightarrow$ $\delta$ 2.93 ($H_{8a}$), $\delta$ 2.77 ($H_{8b}$), $\delta$ 2.05 ($H_{6endo}$), $\delta$ 0.04 ($H_{6exo}$); $\delta$ 2.93 ($H_{8a}$) $\leftrightarrow$ $\delta$ 2.77 ($H_{8b}$); $\delta$ 2.05 ($H_{6endo}$) $\leftrightarrow$ $\delta$ 0.04 ($H_{6exo}$); $^{13}$C NMR (100 MHz, $CDCl_3$, $J$ values from HMQC) $\delta$ 197.9 (s, carbonyl), 136.2 (s, $C_{Ph}$), 133.4 (d, $^1J_{CH}$ = 159 Hz, $C_{Ph}$), 128.7 (d, $^1J_{CH}$ = 164 Hz, $C_{Ph}$), 128.0 (d, $^1J_{CH}$ = 162 Hz, $C_{Ph}$), 100.7 (d, $^1J_{CH}$ = 176 Hz, $C_3$), 99.4 (d, $^1J_{CH}$ = 173 Hz, $C_4$), 98.9 (s, $\underline{C}_5Me_5$), 96.7 (d, $^1J_{CH}$ = 171 Hz, $C_2$), 93.8 (d, $^1J_{CH}$ = 156 Hz, $C_1$), 85.7 (d, $^1J_{CH}$ = 158 Hz, $C_5$), 49.3 (d, $^1J_{CH}$ = 129 Hz, $C_7$), 44.6 (t, $^1J_{CH}$ = 124 Hz, $C_8$), 31.5 (t, $^1J_{CH}$ = 125 Hz, $C_6$), 9.6 (q, $^1J_{CH}$ = 127 Hz, $C_5\underline{Me}_5$); HMQC (300 MHz, $CDCl_3$) $\delta$ 133.4 ($C_{Ph}$) $\leftrightarrow$ $\delta$ 7.54 ($H_{Ph}$); $\delta$ 128.7 ($C_{Ph}$) $\leftrightarrow$ $\delta$ 7.43 ($H_{Ph}$); $\delta$ 128.0 ($C_{Ph}$) $\leftrightarrow$ $\delta$ 7.86 ($H_{Ph}$); $\delta$ 100.7 ($C_3$) $\leftrightarrow$ $\delta$ 6.69 ($H_3$); $\delta$ 99.4 ($C_4$) $\leftrightarrow$ $\delta$ 5.42 ($H_4$); $\delta$ 96.7 ($C_2$) $\leftrightarrow$ $\delta$ 4.86 ($H_2$); $\delta$ 93.8 ($C_1$) $\leftrightarrow$ $\delta$ 4.86 ($H_1$); $\delta$ 85.7 ($C_5$) $\leftrightarrow$ $\delta$ 4.23 ($H_5$); $\delta$ 49.3 ($C_7$) $\leftrightarrow$ $\delta$ 3.60 ($H_7$); $\delta$ 44.6 ($C_8$) $\leftrightarrow$ $\delta$ 2.93 ($H_{8a}$), $\delta$ 2.77 ($H_{8b}$); $\delta$ 31.5 ($C_6$) $\leftrightarrow$ $\delta$ 2.05 ($H_{6endo}$), $\delta$ 0.04 ($H_{6exo}$); $\delta$ 9.6 ($C_5\underline{Me}_5$) $\leftrightarrow$ $\delta$ 1.90 ($C_5\underline{Me}_5$). Electrospray MS $m/z$ calculated for $C_{25}H_{30}CoO$ ($M^+ - BF_4^-$): 405.162864; found: 405.162413 (100%). Analysis calculated for $C_{25}H_{30}BCoF_4O$: C, 61.00; H, 6.14; found: C, 60.789; H, 6.201.



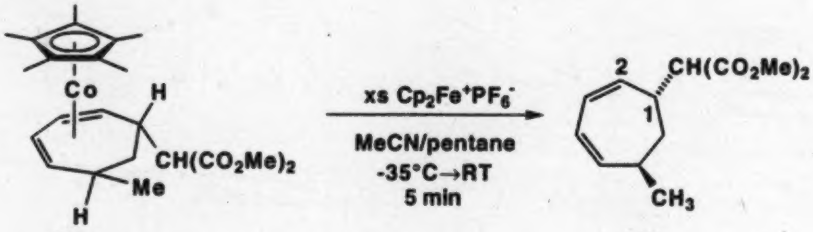
**204** **205**

**Pentamethylcyclopentadienyl[1-(2-5η-6-acetophenone-cyclohepta-2,4-dienyl)malonate] cobalt (205).** To a solution of $[(C_5Me_5)Co(C_7H_8(C_8H_7O))]^+ BF_4^-$ (**204**) (15.1 mg, 30.7 μmol) in tetrahydrofuran (3 mL) at -78°C was added sodium dimethylmalonate (8.7 mg, 1.8 equiv). The light orange solution was allowed to slowly warm to room temperature over 16 h. The tetrahydrofuran solvent was removed *in vacuo* and the residue was extracted with 1:1 benzene/hexane until the extracts were colorless. The combined extracts were filtered through a Celite pad and the solvents were removed. A light orange powder (9.0 mg, 55%) was obtained. IR (benzene cast, $cm^{-1}$) 3003 (w), 2951 (m), 2909(m), 2865 (m), 1745 (m), 1735 (m), 1717 (s), 1681 (s), 1654 (m), 1617 (w), 1597 (w), 1577 (w), 1560 (w), 1446 (m), 1426 (m), 1408 (w), 1383 (m), 1357 (w), 1327 (w), 1316 (w), 1296 (m), 1262 (s), 1206 (s), 1168 (s), 1131 (s), 1096 (s), 1048 (s), 1030 (s), 1011 (s), 992 (s), 967 (m), 916 (m), 868 (w), 801 (s), 751 (s), 684 (s), 588 (w), 502 (m), 466 (m); $^1$H NMR (400 MHz, $C_6D_6$) δ 7.82 (d, $J$ = 6.6 Hz, 2H, $H_{Ph}$), 7.15-7.00 (m, 3H, $H_{Ph}$), 4.04 (dd, $J_{3\text{-}2}$ = 6.9 Hz, $J_{3\text{-}4}$ = 4.5 Hz, 1H, $H_3$), 3.93 (dd, $J_{4\text{-}5}$ = 6.9 Hz, $J_{4\text{-}3}$ = 4.2 Hz, 1H, $H_4$), 3.38 (s, 3H, $CO_2Me$), 3.34 (s, 3H, $CO_2Me$), 3.29 (d, $J_{8\text{-}1}$ = 7.5 Hz, 1H, $H_8$), 2.65 (dd, $J_{9a\text{-}9b}$ = 16.2 Hz, $J_{9a\text{-}6}$ = 8.4 Hz, 1H, $H_{9a}$), 2.54 (dddd, $J_{1\text{-}7exo}$ = 12.3 Hz, $J_{1\text{-}8}$ = 7.2 Hz, $J_{1\text{-}7endo}$ = 3.3 Hz, $J_{1\text{-}2}$ = 1.5 Hz, 1H, $H_1$), 2.42 (dd, $J_{9b\text{-}9a}$ = 16.2 Hz, $J_{9b\text{-}6}$ = 5.1 Hz, 1H, $H_{9b}$), 2.39-2.32 (m, 1H, $H_6$), 2.26 (br d, $J_{2\text{-}3}$ = 6.6 Hz, 1H, $H_2$), 2.18 (br d, $J_{5\text{-}4}$ = 6.9 Hz, 1H, $H_5$), 1.71 (s, 15H, $C_5Me_5$), 1.26-1.19 (m, 1H, $H_{7endo}$), 0.58 (q, $J_{7exo\text{-}7endo} = J_{7exo\text{-}6} = J_{7exo\text{-}1}$ = 12.0 Hz, 1H, $H_{7exo}$); $^1$H-$^1$H GCOSY (300 MHz, $C_6D_6$) δ 7.82 ($H_{Ph}$) ↔ δ 7.07 ($H_{Ph}$); δ 4.04 ($H_3$) ↔ δ 2.26 ($H_2$); δ 3.93 ($H_4$) ↔ δ 2.18 ($H_5$); δ

3.29 ($H_8$) ↔ δ 2.54 ($H_1$); δ 2.65 ($H_{9a}$) ↔ δ 2.42 ($H_{9b}$), δ 2.37 ($H_6$); δ 2.54 ($H_1$) ↔ δ 2.26 ($H_2$), δ 1.23 ($H_{7endo}$), δ 0.58 ($H_{7exo}$); δ 2.37 ($H_6$) ↔ δ 2.18 (w, $H_5$), δ 1.23 ($H_{7endo}$), δ 0.58 ($H_{7exo}$); δ 2.26 ($H_2$) ↔ δ 1.23 ($H_{7endo}$); δ 2.18 ($H_5$) ↔ δ 1.23 ($H_{7endo}$); δ 1.23 ($H_{7endo}$) ↔ δ 0.58 ($H_{7exo}$); $^{13}C$ NMR (100 MHz, $C_6D_6$, *J* values from HMQC spectrum) δ 198.4 (s, C(O)Ph), 169.0 (s, $CO_2Me$), 168.7 (s, $CO_2Me$), 138.1 (s, $C_{Ph,ipso}$), 132.5 (d, $^1J_{CH}$ = 162 Hz, $C_{Ph}$), 128.5 (d, $^1J_{CH}$ = 161 Hz, $C_{Ph}$), 128.3 (d, $^1J_{CH}$ = 161 Hz, $C_{Ph}$), 90.3 (s, $\underline{C}_5Me_5$), 80.7 (d, $^1J_{CH}$ = 164 Hz, $C_4$), 80.6 (d, $^1J_{CH}$ = 165 Hz, $C_3$), 60.1 (d, $^1J_{CH}$ = 134 Hz, $C_8$), 57.2 (d, $^1J_{CH}$ = 144 Hz, $C_5$), 53.1 (d, $^1J_{CH}$ = 146 Hz, $C_2$), 51.6 (q, $^1J_{CH}$ = 147 Hz, $CO_2Me$), 48.8 (t, $^1J_{CH}$ = 133 Hz, $C_9$), 40.0 (d, $^1J_{CH}$ = 131 Hz, $C_1$), 35.9 (d, $^1J_{CH}$ = 126 Hz, $C_6$), 34.3 (t, $^1J_{CH}$ = 126 Hz, $C_7$), 9.5 (q, $^1J_{CH}$ = 126 Hz, $C_5\underline{Me}_5$); HMQC (300 MHz, $C_6D_6$) δ 132.5 ($C_{Ph}$) ↔ δ 7.07 ($H_{Ph}$); δ 128.5 ($C_{Ph}$) ↔ δ 7.82 ($H_{Ph}$); δ 128.3 ($C_{Ph}$) ↔ δ 7.07 ($H_{Ph}$); δ 80.7 ($C_4$) ↔ δ 3.93 ($H_4$); δ 80.6 ($C_3$) ↔ δ 4.04 ($H_3$); δ 60.1 ($C_8$) ↔ δ 3.29 ($H_8$); δ 57.2 ($C_5$) ↔ δ 2.18 ($H_5$); δ 53.1 ($C_2$) ↔ δ 2.26 ($H_2$); δ 51.6 ($CO_2\underline{Me}$) ↔ δ 3.38 ($CO_2\underline{Me}$), δ 3.34 ($CO_2\underline{Me}$); δ 48.8 ($C_9$) ↔ δ 2.65 ($H_{9a}$), δ 2.42 ($H_{9b}$); δ 40.0 ($C_1$) ↔ δ 2.54 ($H_1$); δ 35.9 ($C_6$) ↔ δ 2.37 ($H_6$); δ 34.3 ($C_7$) ↔ δ 1.23 ($H_{7endo}$), δ 0.58 ($H_{7exo}$); δ 9.5 ($C_5\underline{Me}_5$) ↔ δ 1.71 ($C_5\underline{Me}_5$). MS *m/z* calculated for $C_{30}H_{37}CoO_5$ ($M^+$): 536.19733; found: 536.19747 (100%).



**Dimethyl (cyclohepta-2,4-dien-1-yl)malonate (206).** To a cold (-35 °C) slurry of ferricenium hexafluorophosphate (0.1515 g, 0.4577 mmol, 2.6 equiv) in dry acetonitrile (10 mL) was added a solution of $(C_5Me_5)Co(\eta^4\text{-}C_7H_8(CH(CO_2Me)_2))$ (**192**) (0.0725 g, 0.173 mmol) in pentane (15 mL). The cooling bath was removed and the solution was allowed to warm to room temperature. After stirring 5 min, the pentane layer was separated, water (5 mL) was added and the acetonitrile layer was extracted with pentane (3x20 mL). The combined pentane extracts were dried ($MgSO_4$) and the solvents removed on a rotory evaporator. The residue was flash chromatographed on a silica gel column, using 10% ethyl acetate/hexane. A colorless oil was obtained (26 mg, 67%). IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3019 (m), 2954 (m), 2932 (m), 2889 (m), 1754 (s), 1736 (s), 1612 (w), 1435 (s), 1336 (m), 1274 (s), 1260 (s), 1246 (s), 1229 (s), 1198 (s), 1156 (s), 1111 (m), 1056 (m), 1019 (m), 977 (m), 685 (m); $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.8-5.6 (m, 4H, $H_{2-5}$), 3.75 (s, 3H, $CO_2\underline{Me}$), 3.74 (s, 3H, $CO_2\underline{Me}$), 3.51 (d, *J* = 9 Hz, 1H, $H_8$), 3.1-3.2 (m, 1H, $H_{6/7}$), 2.4-2.3 (m, 2H, $H_{6/7}$), 1.9-1.7 (m, 2H, $H_{6/7}$); $^{13}C$ NMR (50 MHz, $CDCl_3$) δ 168.82 ($\underline{C}O_2Me$), 168.76 ($\underline{C}O_2Me$), 134.45 ($C_{2-5}$), 132.94 ($C_{2-5}$), 125.80 ($C_{2-5}$), 124.56 ($C_{2-5}$), 55.78 ($C_8$), 52.47 ($CO_2\underline{Me}$), 40.55 ($C_1$), 29.50 ($C_{6/7}$), 29.23 ($C_{6/7}$). MS *m/z* calculated for $C_{12}H_{16}O_4$ ($M^+$): 224.10486; found: 224.10451(5%); *m/z* calculated for $C_7H_8$ ($M^+$ - dimethyl malonate): 92.06260; found 92.06231 (89%).

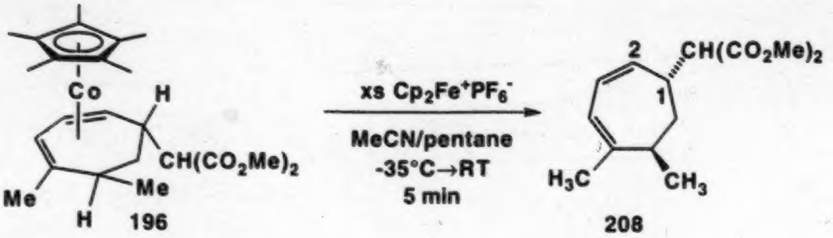


195

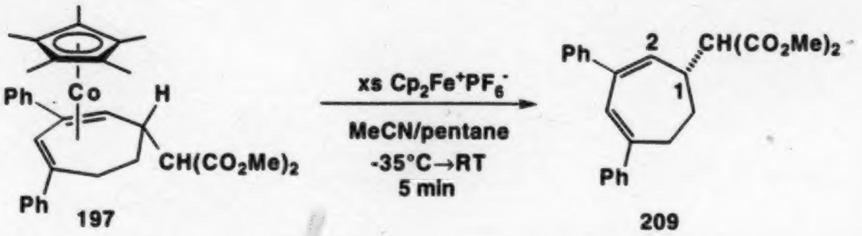
207

**Dimethyl (6-methylcyclohepta-2,4-dien-1-yl)malonate (207).** To a cold (-35 °C) slurry of ferricenium hexafluorophosphate (0.1435 g, 0.4335 mmol, 2.6 equiv) in dry acetonitrile (10 mL) was added a solution of $(C_5Me_5)Co(\eta^4\text{-}6\text{-}Me\text{-}C_7H_7(CH(CO_2Me)_2))$ (**195**) (0.0729 g, 0.169 mmol) in pentane (10 mL). The cooling bath was removed and the solution was allowed to warm to room temperature. After stirring 5 min, the pentane layer was separated, water (5 mL) was added and the acetonitrile layer was extracted with pentane (3x20 mL). The combined pentane extracts were dried ($MgSO_4$) and the solvents removed on a rotory evaporator. The residue was flash chromatographed on a silica gel column, using 5% ethyl acetate/hexane. A colorless oil was obtained (25 mg, 62%). Also isolated by flash chromatography was $(C_5H_5)_2Fe$ (60 mg, 76% from ferricenium hexafluorophosphate, 95% from cobalt diene) as a yellow-orange solid.

The acetonitrile layer was filtered and reduced to 5 mL in volume. The remaining water droplets were removed by pipette. The residue was redissolved in dichloromethane (15 mL) and dried over sodium sulfate. Two volumes of diethyl ether were added and the precipitate of $[(C_5Me_5)Co(NCMe)_3](PF_6)_2$ was collected as a light purple powder (56 mg, 55%). Data for $C_{13}H_{18}O_4$ (**207**): IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3015 (w), 2955 (m), 1756 (s), 1737 (s), 1610 (vw), 1435 (m), 1240 (m), 1194 (m), 1157 (s), 1023 (m), 699 (w), 667 (w); $^1H$ NMR (300 MHz, $CDCl_3$) δ 5.8-5.6 (m, 4H, $H_{2\text{-}5}$), 3.72 (s, 3H, $OCH_3$), 3.71 (s, 3H, $OCH_3$), 3.51 (d, $J = 9.0$ Hz, 1H, $H_8$), 3.12-2.96 (m, 1H, $H_1$), 2.56-2.46 (m, 1H, $H_6$), 1.92-1.64 (m, 2H, $H_7$), 1.04 (d, $J = 7.2$ Hz, 3H, $CH_3$); $^1H\text{-}^1H$ GCOSY (300 MHz, $CDCl_3$) δ 5.70 ($H_{2\text{-}5}$) $\leftrightarrow$ δ 3.05 ($H_1$), δ 2.50 ($H_6$); δ 3.51 ($H_8$) $\leftrightarrow$ δ 3.05 ($H_1$); δ 3.05 ($H_1$) $\leftrightarrow$ δ 1.70 ($H_7$); δ 2.50 ($H_6$) $\leftrightarrow$ δ 1.70 ($H_7$), δ 1.04 ($CH_3$); $^{13}C$ (100 MHz, $CDCl_3$) δ 168.8 (s, $\underline{C}O_2Me$), 140.1 (d, $^1J_{CH} = 150.0$ Hz, $C_{2\text{-}5}$), 133.8 (d, $^1J_{CH} = 160.8$ Hz, $C_{2\text{-}5}$), 125.7 (d, $^1J_{CH} = 144.8$ Hz, $C_{2\text{-}5}$), 122.9 (d, $^1J_{CH} = 161.8$ Hz, $C_{2\text{-}5}$), 56.1 (d, $^1J_{CH} = 135.7$ Hz, $C_8$), 52.4 (q, $^1J_{CH} = 147.4$ Hz, $CO_2\underline{Me}$), 37.2 (d, $^1J_{CH} = 131.1$ Hz, $C_1$), 37.2 (t, $^1J_{CH} = 128.6$ Hz, $C_7$), 33.4 (d, $^1J_{CH} = 122.5$ Hz, $C_6$), 22.0 (q, $^1J_{CH} = 125.2$ Hz, $CH_3$); $^1H\text{-}^{13}C$ HETCORR (100 MHz, $CDCl_3$) δ 140.1 ($C_{3/4}$) $\leftrightarrow$ δ 5.75 ($H_{2\text{-}5}$); δ 133.8 ($C_{3/4}$) $\leftrightarrow$ δ 5.75 ($H_{2\text{-}5}$); δ 125.7 ($C_{2/5}$) $\leftrightarrow$ δ 5.75 ($H_{2\text{-}5}$); δ 122.9 ($C_{2/5}$) $\leftrightarrow$ δ 5.75 ($H_{2\text{-}5}$); δ 56.1 ($C_8$) $\leftrightarrow$ δ 3.51 ($H_8$); δ 37.2 ($C_{1/7}$) $\leftrightarrow$ δ 3.05 ($H_1$), δ 1.75 ($H_7$); δ 33.4 ($C_6$) $\leftrightarrow$ δ 2.50 ($H_6$); δ 22.0 ($CH_3$) $\leftrightarrow$ δ 1.04 ($CH_3$). MS *m/z* calculated for $C_{13}H_{18}O_4$ ($M^+$): 238.12051; found 238.12103 (1%); *m/z* calculated for $C_8H_{10}$ ($M^+$- dimethyl malonate): 106.07825; found: 106.07804 (41%).

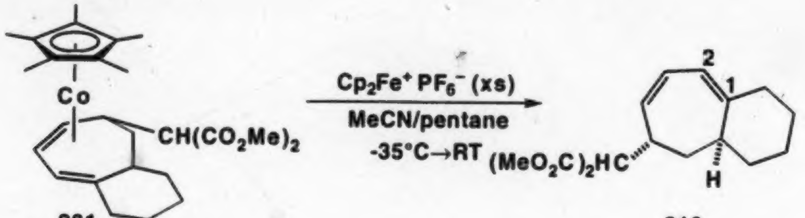


**Dimethyl (5,6-dimethylcyclohepta-2,4-dien-1-yl)malonate (208).** To a cold (-35 °C) slurry of ferricenium hexafluorophosphate (0.1101 g, 0.3326 mmol, 2.2 equiv) in dry acetonitrile (15 mL) was added a solution of $(C_5Me_5)Co(\eta^4\text{-}5,6\text{-}Me_2\text{-}C_7H_6(CH(CO_2Me)_2))$ (**196**) (0.0688 g, 0.154 mmol) in pentane (10 mL). The cooling bath was removed and the solution was allowed to warm to room temperature. After stirring 5 min, the pentane layer was separated, water (5 mL) was added and the acetonitrile layer was extracted with pentane (3x20 mL). The combined pentane extracts were dried ($MgSO_4$) and the solvents removed on a rotory evaporator. The residue was flash chromatographed on a silica gel column, using 10% ethyl acetate/hexane. A colorless oil was obtained (19.2 mg, 49%). IR ($CH_2Cl_2$ cast, $cm^{-1}$) 2957 (s), 2927 (m), 2875 (m), 2853 (m), 1753 (s), 1736 (s), 1617 (w), 1436 (m), 1375 (m), 1335 (m), 1256 (s), 1194 (s), 1158 (s), 1097 (m), 1077 (m), 1019 (m), 718 (m); $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.71 (ddd, $J$ = 11.6, 7.4, 2.6 Hz, 1H, $H_2$), 5.53 (m, 2H, $H_{3,4}$), 3.74 (s, 6H, $CO_2\underline{Me}$), 3.47 (d, 7.9 Hz, 1H, $H_8$), 3.20 (m, 1H, $H_1$), 2.42 (m, 2H, $H_{6/7}$), 1.85 (s, 3H, $Me_5$), 1.73 (m, 2H, $H_{6/7}$, 1.09 (d, $J$ = 7.1 Hz, 3H, $Me_6$); $^{13}C$ NMR (75 MHz, $CD_2Cl_2$) δ 169.3 (s, $\underline{C}O_2Me$), 148.5 (s, $C_5$), 131.8 (d, $^1J_{CH}$ = 154 Hz, $C_2$), 125.5 (d, $^1J_{CH}$ = 154 Hz, $C_{3/4}$), 119.9 (d, $^1J_{CH}$ = 146 Hz, $C_{3/4}$), 57.0 (d, $J_{CH}$ = 131 Hz, $C_8$), 52.6 (q, $J_{CH}$ = 147 Hz, overlapped with solvent, $CO_2\underline{Me}$), 38.0[a] (t, $J_{CH}$ = 121 Hz, $C_7$), 37.1 (d, $J_{CH}$ = 126 Hz, $C_6$), 35.5[a] (d, $J_{CH}$ = 135 Hz, $C_1$), 25.3 (q, $J_{CH}$ = 129 Hz, $Me_5$), 18.6 (q, $J_{CH}$ = 127 Hz, $Me_6$). [a] peaks overlap; $J$'s are somewhat inaccurate. MS $m/z$ calculated for $C_{14}H_{20}O_4$ ($M^+$): 252.13615; found: 252.13602 (6%), $m/z$ calculated for $C_9H_{12}$ ($M^+$- dimethyl malonate): 120.09390; found: 120.09384 (100%).



**Dimethyl (3,5-diphenylcyclohepta-2,4-dien-1-yl)malonate (209).** To a cold (-35 °C) slurry of ferricenium hexafluorophosphate (33.9 mg, 0.102 mmol, 2.6 equiv) in dry acetonitrile (8 mL) was added a solution of $(C_5Me_5)Co(\eta^4\text{-}3,5\text{-}Ph_2\text{-}C_7H_8(CH(CO_2Me)_2))$ (**197**) (22.7 mg, 0.040 mmol) in pentane (10 mL). The cooling bath was removed and the solution was allowed to warm to room temperature. After stirring 5 min, the pentane layer was separated, water (5 mL) was added and the acetonitrile layer was extracted with pentane (3x10 mL). The combined pentane extracts were dried ($MgSO_4$) and the solvents removed on a rotory evaporator. The residue was flash chromatographed on a silica gel column, using pentane to elute ferrocene, then using dichloromethane to elute the desired product. A colorless oil was obtained (7.5 mg, 50%). IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3024 (m), 2952 (m), 2925 (m), 2853 (m), 1754 (s), 1736 (s), 1598 (w), 1492 (m), 1445 (m), 1434 (s), 1364 (m), 1281 (m), 1252 (s), 1219 (m), 1195 (s), 1156 (s), 1132 (m), 1107 (m), 1076 (m), 1028 (m), 757 (s), 698 (s); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.52-7.27 (m, 10H, $H_{phenyl}$), 6.49 (s, 1H, $H_4$), 6.35 (d, $J_{2\text{-}1}$ = 5.7 Hz, 1H, $H_2$), 3.79 (s, 3H, $OCH_3$), 3.76 (s, 3H, $OCH_3$), 3.62 (d, $J$ = 8.2 Hz, 1H, $H_8$), 3.21 (m, 1H, $H_1$), 2.66 (m, 2H, $H_{6/7}$), 2.40 (m, 1H, $H_{6/7}$), 2.19 (m, 1H, $H_{6/7}$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 169.1 ($\underline{C}O_2Me$), 146.9 ($C_{2\text{-}5}$), 142.8 ($C_{2\text{-}5}$), 141.5 ($C_{2\text{-}5}$), 140.6 ($C_{2\text{-}5}$), 130.3 ($C_{phenyl}$), 128.5 ($C_{phenyl}$), 128.4 ($C_{phenyl}$), 127.5 ($C_{phenyl}$), 127.4 ($C_{phenyl}$), 126.9 ($C_{phenyl}$), 126.7 ($C_{phenyl}$), 126.3 ($C_{phenyl}$), 55.8 ($C_8$), 52.6 ($CO_2\underline{Me}$), 40.0 ($C_1$), 38.8 ($C_{6/7}$), 30.4 ($C_{6/7}$). MS *m/z* calculated for $C_{24}H_{24}O_4$ ($M^+$): 376.16745; found:

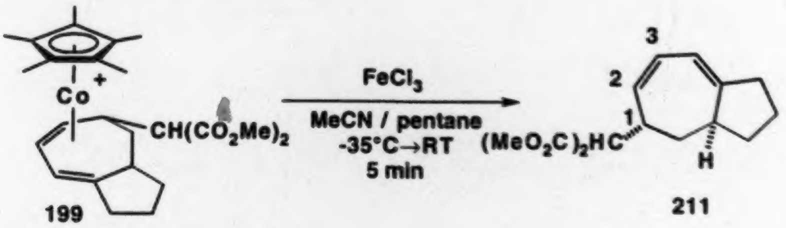
376.16704 (9%); *m/z* calculated for $C_{19}H_{16}$ ($M^+$ - dimethyl malonate): 244.12520; found: 244.12507 (100%).



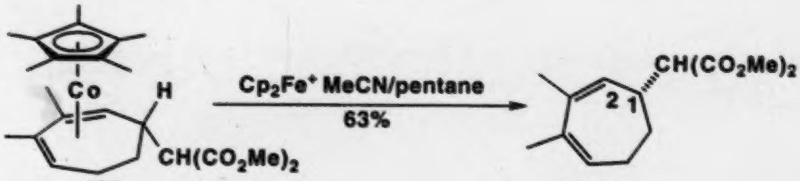
201 210

**Dimethyl(bicyclo[5.4.0]undeca-1,3-dien-5-yl)malonate. 5-(bis(carbomethoxy)methyl)bicyclo[5.4.0]undeca-1,3-diene (210).** In the drybox, a Schlenk flask was charged with [($C_5Me_5$)Co($\eta^4$-5-(bis(carbomethoxy) methyl) bicyclo[5.4.0]undeca-1,3-diene)] (**201**) (67.9 mg, 0.144 mmol) and pentane (20 mL) was then added. This solution was cannula transferred into a cooled (-30 °C) solution of ferricinium hexafluorophosphate (0.1262 g, 2.6 equiv) in acetonitrile (20 mL). The cooling bath was then removed and the solution was warmed to room temperature. The acetonitrile layer was then separated, and extracted with pentane (5 x 30 mL). The combined pentane extracts were washed with water (2 x 10 mL) and dried ($Na_2SO_4$). The pentane was removed under reduced pressure. The residue was then flash chromatographed on silica gel using pentane. Once the ferrocene was eluted, the eluent was changed to 5% ethyl acetate-hexane and the product was eluted. The solvent was removed, leaving 25.0 mg (0.0898 mmol, 62%) of a slightly yellow oil. IR (hexane cast, $cm^{-1}$) 3024 (w), 2998 (w), 2949 (s), 2927 (s), 2853 (m), 1756 (s), 1737 (s), 1616 (w), 1435 (s), 1337 (m), 1262 (s), 1242 (s), 1221 (s), 1194 (s), 1157 (s), 1111 (m), 1073 (w), 1055 (w), 1020 (m), 991 (w), 969 (w), 866 (w), 796 (w), 728 (w), 714 (w), 683 (w); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 5.70-5.65 (m, 2H, $H_{2,4}$), 5.60- 5.56 (m, 1H, $H_3$), 3.74 (s, 3H, $CO_2\underline{Me}$), 3.72 (s, 3H, $CO_2\underline{Me}$), 3.55 (d, $J_{12\text{-}5}$ = 9.4 Hz, $H_{12}$), 3.08 (br t, $J$ = 8.7 Hz, 1H, $H_5$), 2.35-2.05 (m, 3H, $CH_2$, $H_7$), 1.92-1.75 (m, 3H, $H_6$, $CH_2$), 1.70-1.53 (m, 3H, $H_6$, $CH_2$), 1.50-1.20 (m, 2H, $CH_2$); $^1H$-$^1H$ GCOSY (300 MHz, $CDCl_3$) $\delta$ 5.65 ($H_4$) $\leftrightarrow$ $\delta$

3.08 ($H_5$); δ 3.55 ($H_{12}$) ↔ δ 3.08 ($H_5$); δ 3.08 ($H_5$) ↔ δ 1.85 ($H_{6endo}$), δ 1.64 (w, $H_{6exo}$); δ 2.35 ($CH_2$) ↔ δ 1.85 ($CH_2$), δ 1.64 ($CH_2$), δ 1.44 ($CH_2$); δ 2.15 ($CH_2$) ↔ δ 1.85 ($CH_2$); δ 1.85 ($CH_2$) ↔ δ 1.64 ($CH_2$); δ 1.80 ($CH_2$) ↔ δ 1.44 ($CH_2$); δ 1.64 ($CH_2$) ↔ δ 1.44 ($CH_2$); $^{13}C$ NMR (300 MHz, $CDCl_3$) δ 168.97 (s, $\underline{C}O_2Me$), 168.89 (s, $\underline{C}O_2Me$), 149.8 (s, $C_1$ ), 132.7 (d, $^1J_{CH}$ = 160.1 Hz, $C_{2/3}$), 125.7 (dd, $^1J_{CH}$ = 155.0 Hz, $^2J_{CH}$ = 5.2 Hz, $C_{2,3}$), 118.4 (d, $^1J_{CH}$ = 148.0 Hz, $C_4$), 55.3$^a$ (d, $^1J_{CH}$ = 132.6 Hz, $C_{12}$), 52.4$^a$ (q, $^1J_{CH}$ = 147.5 Hz, $CO_2\underline{Me}$), 42.2 (d, $^1J_{CH}$ = 125.1 Hz, $C_7$), 39.5 (t, $^1J_{CH}$ = 127.0 Hz, $CH_2$), 37.1 (t, $^1J_{CH}$ = 126.0 Hz, $CH_2$), 36.8 (d, $^1J_{CH}$ = 118.6 Hz, $C_5$), 36.6 (t, $^1J_{CH}$ = 127.5 Hz, $CH_2$), 28.8 (t, $^1J_{CH}$ = 128.4 Hz, $CH_2$), 26.7 (t, $^1J_{CH}$ = 124.6 Hz, $CH_2$); $^1H$-$^{13}C$ HETCORR (100 MHz, $CDCl_3$) δ 132.7 ($C_{2,3}$) ↔ δ 5.67 ($H_{2,3}$); δ 125.7 ($C_{2,3}$) ↔ δ 5.69 ($H_{2,3}$); δ 118.4 ($C_4$) ↔ δ 5.57 ($H_4$); δ 55.3 ($C_{12}$) ↔ δ 3.55 ($H_{12}$); δ 52.4 ($CO_2\underline{Me}$) ↔ δ 3.74 ($CO_2\underline{Me}$), δ 3.72 ($CO_2\underline{Me}$); δ 42.2 ($C_7$) ↔ δ 2.35 ($H_7$); δ 39.5 ($CH_2$) ↔ δ 2.2 ($CH_2$), δ 2.1 ($CH_2$); δ 37.1 ($CH_2$) ↔ δ 1.75 ($CH_2$), δ 1.65 ($CH_2$); δ 36.8 ($C_5$) ↔ δ 3.08 ($H_5$); δ 36.6 ($CH_2$) ↔ δ 1.65 ($CH_2$), δ 1.4 ($CH_2$); δ 28.8 ($CH_2$) ↔ δ 1.85 ($CH_2$), δ 1.45 ($CH_2$); δ 26.7 ($CH_2$) ↔ δ 1.80 ($CH_2$), δ 1.50 ($CH_2$); MS *m/z* calculated for $C_{16}H_{22}O_4$ ($M^+$): 278.15179; found: 278.15107 (7%).



**Dimethyl(bicyclo[5.3.0]deca-1,3-dien-5-yl)malonate. 5-(bis(carbomethoxy)methyl)bicyclo[5.3.0]deca-1,3-diene (211).** A Schlenk flask was charged with a solution of $(C_5Me_5)Co(C_{15}H_{19}O_4)$ (**199**) (35.6 mg, 77.8 μmol) in pentane (20 mL). This solution was added dropwise to a stirred solution of ferric chloride (31.6 mg, 2.5 equiv) in acetonitrile (10 mL) at -30°C. The resulting two phase system was held at -30°C for 5 min, after which a complete loss of color from the pentane layer was observed. The mixture was stirred at room temperature for an additional 5 min before the pentane layer was removed and the acetonitrile was extracted with pentane (3x15 mL). The combined pentane extracts were washed with water (5 mL), dried ($Na_2SO_4$) and the solvent was removed on the rotory evaporator. A pale yellow oily material (14.0 mg, 39%) was obtained. IR ($CH_2Cl_2$ cast, $cm^{-1}$) 2957 (s), 2867 (m), 1750 (s), 1736 (s), 1658 (w), 1615 (w), 1435 (s), 1262 (s), 1194 (s), 1150 (s), 1096 (s), 1022 (s), 864 (m), 801 (s), 740 (m), 705 (m); $^1H$ NMR (300 MHz, $CDCl_3$) δ 5.81 (dd, *J* = 11.7, 6.9 Hz, 1H, $H_3$), 5.68 (ddd, *J* = 6.9, 2.4, 2.4 Hz, 1H, $H_4$), 5.60 (dd, *J* = 11.7, 6.3 Hz, 1H, $H_2$), 3.73 (s, 3H, $CO_2Me$), 3.73 (s, 3H, Me), 3.41 (d, *J* = 10.5 Hz, 1H, $H_8$), 3.22-3.13 (m, 1H, $H_1$), 2.50-2.37 (m, 2H, $CH_2$), 1.95-1.85 (m, 2H, $CH_2$) 1.80-1.25 (series of m, $CH_2$); $^1H$-$^1H$ GCOSY (300 MHz, $CDCl_3$) δ 5.81 ($H_3$) ↔ δ 5.68 ($H_4$), 3.17 (w, $H_1$); δ 5.68 ($H_4$) ↔ δ 2.43 ($H_6$); δ 5.60 ($H_2$) ↔ δ 3.17 ($H_1$), δ 2.43 ($H_6$), δ 1.90 ($CH_2$); δ 3.41 ($H_8$) ↔ δ 3.17 ($H_1$); δ 3.17 ($H_1$) ↔ δ 1.90 ($CH_2$), 1.75 ($CH_2$); δ 2.43 ($H_6$) ↔ δ 1.90 ($CH_2$), δ 1.75 ($CH_2$), δ 1.25 ($CH_2$); δ 1.90 ($CH_2$) ↔ δ 1.75 ($CH_2$), 1.25 ($CH_2$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 168.6, 168.4, 154.4, 129.4, 126.6, 116.0, 57.4, 52.5, 41.2, 39.2, 35.3, 34.7, 34.4, 25.3; MS *m/z* calculated for $C_{15}H_{20}O_4$ ($M^+$): 264.13617; found: 264.13608 (4.3%); MS *m/z* calculated for $C_{10}H_{12}$ ($M^+$ - dimethylmalonate): 132.09390; found: 132.09366 (52.1%).



194

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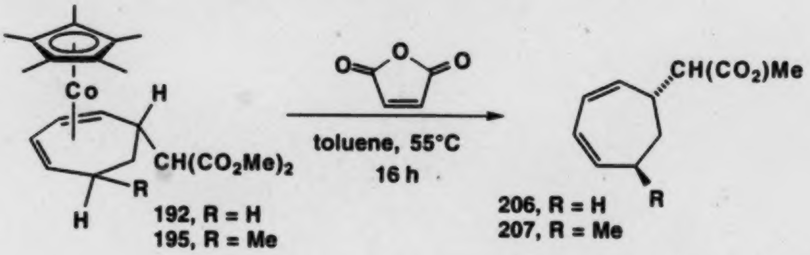
**Dimethyl (3,4-dimethylcyclohepta-2,4-dien-1-yl)malonate (212).** To a cold (-35 °C) slurry of ferricenium hexafluorophosphate (0.107 g, 0.323 mmol, 2.8 equiv) in dry acetonitrile (20 mL) was added a solution of ($C_5Me_5$)Co($\eta^4$-3,4-$Me_2C_7H_8$[CH($CO_2Me$)$_2$]) (**194**) (0.0510 g, 0.114 mmol) in pentane (10 mL). The cooling bath was removed and the solution was allowed to warm to room temperature. After stirring 10 min, the pentane layer was separated, water (5 mL) was added and the acetonitrile layer was extracted with pentane (3x15 mL). The combined pentane extracts were washed with water (5 mL), dried ($MgSO_4$) and the solvents removed on a rotory evaporator. The residue was flash chromatographed on a silica gel column, using hexane to elute ferrocene. The product was then eluted using 20% ethyl acetate/hexane. A colorless oil was obtained (26 mg, 90%). The product was impure by $^1H$ NMR, giving an estimated yield of about 63%. IR (hexane cast, $cm^{-1}$) 2953 (m), 2936 (m), 2855 (w), 1757 (s), 1737 (s), 1620 (vw), 1435 (m), 1371 (w), 1340 (w), 1316 (m), 1267 (m), 1241 (m), 1216 (m), 1201 (m), 1158 (m), 1138 (m), 1068 (w), 1020 (w), 987 (w), 974 (w), 811 (w); $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.83 (ddd, $J$ = 5.8, 6.6, 1.5 Hz, 1H, $H_5$), 5.61 (dd, $J$ = 5.8, 1.4 Hz, 1H, $H_2$), 3.72 (s, 3H, $CO_2Me$), 3.71 (s, 3H, $CO_2Me$), 3.43 (d, $J$ = 8.6 Hz, 1H, $H_8$), 2.87-2.78 (m, ddtd by decoupling), 1H, $H_1$), 2.04 (tt, $J$ = 11.3, 6.9 Hz, 1H, $H_6$), 1.95-1.75 (m, 3H, $H_{methylene}$), 1.76 (s, 3H, Me), 1.75 (s, 3H, Me); Decoupling Irr δ 5.83 ($H_5$) ↔ δ 1.8 (m, changes, $H_{methylene}$); Irr δ 5.61 ($H_2$) ↔ δ 2.82 (m, changes, $H_1$); Irr δ 3.43 ($H_8$) ↔ δ 2.82 (dtd, $J$ = 11.6, 6.9, 1.4 Hz, $H_1$); Irr δ 2.82 ($H_1$) ↔ δ 5.61 (s, $H_2$), 3.43 (s, $H_8$), 2.04 (m, $H_6$); Irr δ 2.04 ($H_6$) ↔ δ 2.82 (m, $H_1$), 1.9 (m, $H_{methylene}$), 1.8 (m, $H_{methylene}$); Irr δ 1.9 ($H_{methylene}$) ↔ δ 5.83 (s, $H_5$), 2.82 (m, $H_1$), 2.04 (m, $H_6$); Irr δ 1.8 ($H_{methylene}$) ↔ δ 5.83 (dd, $H_5$), 5.61 (d, $H_2$), 2.82 (m, $H_{methylene}$), 2.04 (m, $H_6$), 1.9 (m, $H_{methylene}$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 169.2 (br s, $\underline{C}O_2Me$), 139.1 (br s, $C_{3/4}$), 138.8 (br s, $C_{3/4}$), 127.6 (d, $^1J_{CH}$ = 154.2 Hz, $C_5$), 127.3 (d, $^1J_{CH}$ = 149.8 Hz, $C_2$), 55.7 (d, $^1J_{CH}$ = 137.2 Hz, $C_8$), 52.3 (q, $^1J_{CH}$ = 147.7 Hz, $CO_2\underline{Me}$), 40.3 (t, $^1J_{CH}$ = 125.7 Hz, $C_6$), 37.4 (d, $^1J_{CH}$ = 134.6 Hz, $C_1$), 25.2 (t, $^1J_{CH}$ = 126.7 Hz, $C_7$), 20.9 (qd, $^1J_{CH}$ = 126.2, $^3J_{CH}$ = 7.1 Hz, Me), 20.79 (qd, $^1J_{CH}$ = 125.9, 6.7 Hz, Me); $^1H$-$^{13}C$ HETCORR (100 MHz, $CDCl_3$) δ 127.6 ($C_5$) ↔ δ 5.83 ($H_5$); δ 127.3 ($C_2$) ↔ δ 5.61 ($H_2$); δ 55.7 ($C_8$) ↔ δ 3.43 ($H_8$); δ 52.3 ($CO_2\underline{Me}$) ↔ δ 3.72 ($CO_2\underline{Me}$), δ 3.71 ($CO_2\underline{Me}$); δ 40.3 ($C_6$) ↔ δ 2.04 ($H_{methylene}$), δ 1.75 ($H_{methylene}$); δ 37.4 ($C_1$) ↔ δ 2.83 ($H_1$); δ 25.2 ($C_7$) ↔ δ 1.7-

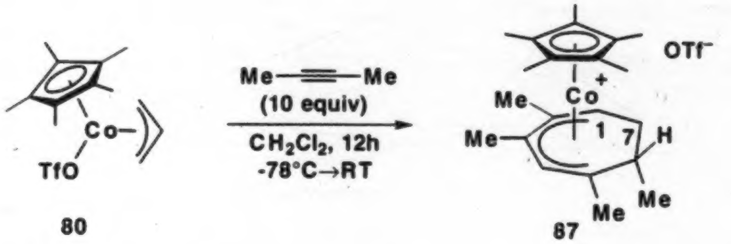
1.9[a] ($H_8$); δ 20.9/20.7[b] (Me) ↔ δ 1.7 (Me); [a] C correlated to a large range in the $^1$H axis [b] resolution was not sufficient to distinguish either C signals or H signals. MS *m/z* calculated for $C_{14}H_{20}O_4$ ($M^+$): 252.13615; found: 252.13625(18%) *m/z* calculated for $C_9H_{12}$ ($M^+$ - malonate): 120.09390; found 120.09411 (100%).



**Dimethyl (cyclohepta-2,4-dien-1-yl)malonate (206).** To a solution of cobalt cycloheptadiene complex **192** (48.7 mg, 0.116 mmol) in dry, degassed toluene (10 mL) was added maleic anhydride (57 mg, 5 equiv). The red solution slowly darkened to a deep red-purple color. The solution was heated to 55°C overnight under a nitrogen atmosphere. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with 10% ethyl acetate/hexanes. A slightly yellow oil (24 mg, 92%) was obtained, although by $^1$H NMR spectroscopy, the compound was not entirely pure. $^1$H NMR spectroscopic analysis showed the material is identical to that isolated from the ferricinium oxidation of complex **192**.

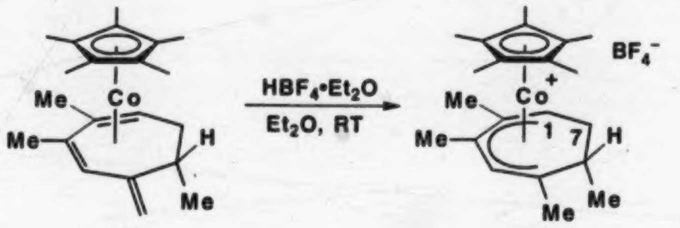
**Dimethyl (6-methylcyclohepta-2,4-dien-1-yl)malonate (207).** To a solution of cobalt cycloheptadiene complex **195** (97.7 mg, 0.219 mmol) in dry, degassed toluene (10 mL) was added maleic anhydride (107 mg, 5 equiv). The red solution slowly darkened to a deep red-purple color. The solution stirred at room temperature overnight under a nitrogen atmosphere. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with 10% ethyl acetate/hexanes. A slightly yellow oil (26 mg, 47%) was obtained. $^1$H NMR spectroscopic analysis showed the material is identical to that isolated from the ferricinium oxidation of complex **195**.

# Chapter 4 Experimental Section



**[$(C_5Me_5)Co(2,3,5,6\text{-}Me_4\text{-}\eta^5\text{-}C_7H_5)]^+$ $TfO^-$ (87).** This complex has previously been prepared and characterized.[88] In the drybox, $(C_5Me_5)Co(\eta^3\text{-}C_3H_5)(OTf)$ (**80**) (315.3 mg, 0.8205 mmol) was placed in a flask equipped with a Kontes value. This flask was removed to the Schlenk line and dichloromethane (10 mL) was added. On the high vacuum line, 2-butyne (0.44 g, 8.2 mmol) was added by vacuum transfer. The solution was warmed to -78 °C, and then allowed to warm slowly to room temperature while being stirred overnight. The solvent was evaporated, the residue washed with diethyl ether and then dissolved in dichloromethane and filtered through Celite. Evaporation gave a red, impure solid (327.3 mg, 81%). The material could be partially purified by dissolving in a minimum amount of dichloromethane and adding dropwise to an excess of rapidly stirring diethyl ether. IR ($CH_2Cl_2$ cast, $cm^{-1}$) 2968 (m), 2912 (m), 1477 (m), 1456 (m), 1434 (m), 1383 (m), 1268 (s), 1221 (m), 1144 (s), 1030 (s), 636 (s), 571 (m), 516 (m); $^1H$ NMR (400 MHz, acetone-$d_6$) $\delta$ 5.10 (br s, 1H, $H_4$), 4.09 (t, $J_{1\text{-}7endo} = J_{1\text{-}7exo} = 4$ Hz, 1H, $H_1$), 2.39 (ddd, $J_{7endo\text{-}1} = 4$ Hz, $J_{7endo\text{-}7exo} = 15.7$ Hz, $J_{7endo\text{-}6endo} = 9.5$ Hz, 1H, $H_{7endo}$), 2.33 (s, 3H, $Me_3$), 1.97 (s, 3H, $Me_2$), 1.88 (m, 1H, $H_{7exo}$, obscured), 1.77 (s, 15H, $C_5\underline{Me_5}$), 1.50 (s, 3H, $Me_5$), 0.99 (d, $J = 6.8$, 3H, $Me_6$), 0.75 (m, 1H, $H_{6endo}$); $^{13}C$ NMR (100 MHz, acetone-$d_6$) $\delta$ 119.4 (s, $C_5$), 106.2 (s, $C_3$ or $C_2$), 106.1 (s, $C_3$ or $C_2$), 98.1 (d, $J_{C\text{-}H} = 162$ Hz, $C_4$), 97.1 (s, $\underline{C_5}Me_5$), 80.6 (d, $J_{C\text{-}H} = 149$ Hz, $C_1$), 49.5 (t, $J_{C\text{-}H} = 128$ Hz, $C_7$), 38.2 (d, $J_{C\text{-}H} = 124$ Hz, $C_6$), 23.3 (q, $J_{C\text{-}H} = 126$ Hz, $Me_5$), 19.8 (q, $J_{C\text{-}H} = 128$ Hz, $Me_2$), 18.2 (q, $J_{C\text{-}H} = 128$ Hz, $Me_3$), 17.2 (q, $J_{C\text{-}H} = 128$ Hz,

$Me_6$), 8.6 (q, $J_{C\text{-}H}$ = 128 Hz, $C_5\underline{Me}_5$). Full characterization on the $BF_4^-$ complex is described below.



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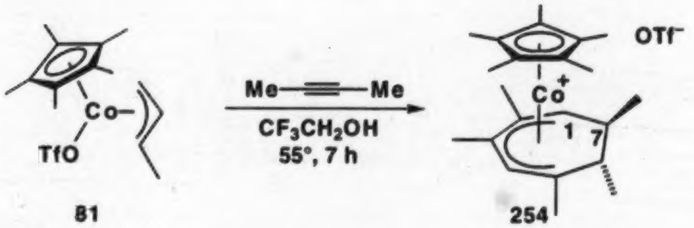
**$[(C_5Me_5)Co(2,3,5,6\text{-}Me_4\text{-}\eta^5\text{-}C_7H_5)]^+ BF_4^-$ (87-$BF_4^-$).** This complex has previously been prepared and spectroscopically characterized.[88] In the drybox, a solution of $[(C_5Me_5)Co(\eta^4$-2,3,6-trimethyl-5-methylene-cyclohepta-1,3-diene)] (**88**) (78.5 mg, 0.229 mmol) in diethyl ether (6 mL) was placed in a Schlenk flask capped with a rubber septum. The flask was removed to the Schlenk line and tetrafluoroboric acid-diethyl ether complex (40 μL, 0.231 mmol) was added with stirring. The orange precipitate (98.6 mg, 100%) was collected and washed with diethyl ether. $^1$H NMR (400 MHz, acetone-$d_6$) δ 5.10 (br s, 1H, $H_4$), 4.09 (t, $J_{1\text{-}7exo} = J_{1\text{-}7endo}$ = 4.4 Hz, 1H, $H_1$), 2.39 (ddd, $J_{7endo\text{-}1}$ = 4 Hz, $J_{7endo\text{-}7exo}$ = 15.7 Hz, $J_{7endo\text{-}6endo}$ = 9.5 Hz, 1H, $H_{7endo}$), 2.33 (s, 3H, $Me_3$), 1.97 (s, 3H, $Me_2$), 1.87 (ddd, $J_{7exo\text{-}7endo}$ = 15.8 Hz, $J_{7exo\text{-}1}$ = 4.5 Hz, $J_{7exo\text{-}6endo}$ = 4.5 Hz, 1H, $H_{7exo}$), 1.77 (s, 15H, $C_5\underline{Me}_5$), 1.50 (s, 3H, $Me_5$), 0.99 (d, $J$ = 6.8, 3H, $Me_6$), 0.74 (m, 1H, $H_{6endo}$); $^1$H-$^1$H COSY (400 MHz, $CD_2Cl_2$, shifts corrected to acetone values) δ 5.10 ($H_4$) ↔ δ 2.39 ($H_{7endo}$), δ 1.50 ($Me_5$); δ 4.09 ($H_1$) ↔ δ 2.39 ($H_{7endo}$), δ 1.87 ($H_{7exo}$); δ 2.39 ($H_{7endo}$) ↔ δ 1.87 ($H_{7exo}$), δ 0.74 ($H_{6endo}$); δ 1.87 ($H_{7exo}$) ↔ δ 0.74 ($H_{6endo}$); δ 0.99 ($Me_6$) ↔ δ 0.74 ($H_{6endo}$); $^{13}$C NMR (100 MHz, acetone-$d_6$) δ 119.9 (s, $C_5$), 106.7 (s, $C_3$ or $C_2$), 106.5 (s, $C_3$ or $C_2$), 98.5 (d, $J_{C\text{-}H}$ = 174 Hz, $C_4$), 97.6 (s, $\underline{C}_5Me_5$), 81.0 (d, $J_{C\text{-}H}$ = 149 Hz, $C_1$), 49.9 (t, $J_{C\text{-}H}$ = 125 Hz, $C_7$), 38.6 (d, $J_{C\text{-}H}$ = 129 Hz, $C_6$), 23.8 (q, $J_{C\text{-}H}$ = 128 Hz, $Me_5$), 20.2 (q, $J_{C\text{-}H}$ = 128 Hz, $Me_2$), 18.6 (q, $J_{C\text{-}H}$ = 128 Hz, $Me_3$), 17.6 (q, $J_{C\text{-}H}$ = 126 Hz, $Me_6$), 9.0 (q, $J_{C\text{-}H}$ = 128 Hz, $C_5\underline{Me}_5$); $^1$H-$^{13}$C

HETCORR (100 MHz, acetone-$d_6$) δ 98.5 ($C_4$) ↔ δ 5.10 ($H_4$); δ 81.0 ($C_1$) ↔ δ 4.09 ($H_1$); δ 49.9 ($C_7$) ↔ δ 2.39 ($H_{7endo}$), δ 1.87 ($H_{7exo}$); δ 38.6 ($C_6$) ↔ δ 0.74 ($H_{6endo}$); δ 23.8 ($Me_5$) ↔ δ 1.50 ($Me_5$); δ 20.2 ($Me_2$) ↔ δ 1.97 ($Me_2$); δ 18.6 ($Me_3$) ↔ δ 2.33 ($Me_3$); δ 17.6 ($Me_6$) ↔ δ 0.99 ($Me_6$); δ 9.0 ($C_5\underline{Me_5}$) ↔ δ 1.77 ($C_5\underline{Me_5}$); $^1H$-$^{13}C$ Long Range HETCORR (100 MHz, acetone-$d_6$) δ 119.9 ($C_5$) ↔ δ 5.10 ($H_4$, very weak), δ 1.50 ($Me_5$), δ 0.99 ($Me_6$); δ 106.7 ($C_3$ or $C_2$) ↔ δ 2.33 ($Me_3$), δ 1.97 ($Me_2$); δ 106.5 ($C_3$ or $C_2$) ↔ δ 5.10 ($H_4$, weak), δ 2.33 ($Me_3$), δ 1.97 ($Me_2$); δ 98.5 ($C_4$) ↔ δ 2.33 ($Me_3$, weak), δ 1.50 ($Me_5$); δ 97.6 ($\underline{C}_5Me_5$) ↔ δ 1.77 ($C_5\underline{Me_5}$); δ 81.0 ($C_1$) ↔ δ 1.97 ($Me_2$); δ 49.9 ($C_7$) ↔ δ 0.99 ($Me_6$); δ 38.6 ($C_6$) ↔ δ 1.50 ($Me_5$), δ 0.99 ($Me_6$); δ 23.8 ($Me_5$) ↔ δ 5.10 ($H_4$); δ 20.2 ($Me_2$) ↔ δ 4.09 ($H_1$). Analysis calculated for $C_{21}H_{32}CoBF_4$: C, 58.63; H, 7.50; found: C, 58.47; H, 7.49.

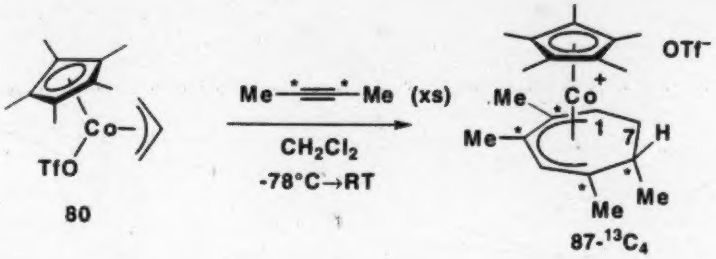


**[($C_5Me_5$)Co($\eta^5$-2,3,5,6,7-$Me_5C_7H_4$)]$^+$ OTf$^-$ (252)**. In the drybox, ($\eta^5$-$C_5Me_5$)Co($\eta^3$-1-Me-$C_3H_4$)(OTf) (**81**) (0.0811g, 0.204 mmol) was weighed out into a small vessel equipped with a Kontes valve. 2,2,2-Trifluoroethanol (about 4 mL) was added to the flask to produce a dark brown suspension, which slowly dissolved. 2-Butyne (0.2 mL, about 10 equiv) was added by pipette and the valve was sealed. The solution was heated to 55 °C for 7 h, giving a dark red solution and then cooled to room temperature. All volatile material was removed *in vacuo* and the residue was purified by flash chromatography on a silica gel column. The deep red product was eluted with 7% methanol/dichloromethane. Recrystallization from dichloromethane/diethyl ether gave a dark red solid (60 mg, 58%). An addditional 21 mg (total 78%) was recovered from the mother liquor. IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3058 (w), 2971 (m), 2913 (m), 2873 (w), 1492 (w), 1453 (m), 1434 (m), 1384 (m), 1268 (s), 1222 (s), 1145 (m), 1073 (w), 1031 (s), 1014 (m), 735 (s), 702 (m), 637 (s), 571 (w), 517 (m); $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 4.91 (s, 1H, $H_4$), 3.78 (d, $J_{1\text{-}7exo}$ = 3.0 Hz, 1H, $H_1$), 2.56 (dqd, $J_{7exo\text{-}6endo}$ = 10.0 Hz, $J_{7exo\text{-}methyl}$ = 6.7 Hz, $J_{7exo\text{-}1}$ = 3.1 Hz, 1H, $H_{7exo}$), 2.21 (s, 3H, Me), 1.82 (s, 3H, Me), 1.66 (s, 15H, $C_5\underline{Me}_5$), 1.38 (s, 3H, Me), 0.89 (d, $J$ = 6.7 Hz, 3H, $Me_7$), 0.85 (d, $J$ = 6.8 Hz, 3H, $Me_6$), -0.12 (dq, $J_{6endo\text{-}7exo}$ = 10.0 Hz, $J_{6endo\text{-}methyl}$ = 7.0 Hz, 1H, $H_{6endo}$); $^1$H-$^1$H COSY (400 MHz, $CD_2Cl_2$) δ 3.78 ($H_1$) ↔ δ 2.56 ($H_{7exo}$); δ 2.56 ($H_{7exo}$) ↔ δ 0.89 ($Me_7$); δ 0.85 ($Me_6$) ↔ δ –0.12 ($H_{6endo}$); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) δ 121.4 (q, $^1J_{CF}$ = 321.3 Hz, triflate carbon), 117.9 (s, $C_3$), 106.2 (s, $C_{2/5}$), 103.3 (s, $C_{2/5}$), 98.0 (d, $^1J_{CH}$ = 177 Hz, obscured by $\underline{C}_5Me_5$, $C_4$), 97.0 (s, $\underline{C}_5Me_5$), 87.0 (d, $^1J_{CH}$ = 145.6 Hz, $C_1$), 59.4 (d, $^1J_{CH}$ = 131.8 Hz, $C_7$), 41.0 (d, $^1J_{CH}$ = 130.7 Hz, $C_6$), 23.1 (q, $^1J_{CH}$ = 125.9 Hz, Me), 22.6 (q, $^1J_{CH}$ = 127.3 Hz, $Me_7$), 21.2 (q, $^1J_{CH}$ = 128.3 Hz, Me), 18.6 (q, $^1J_{CH}$ = 129.4 Hz, Me), 15.7 (q, $^1J_{CH}$ = 127.4 Hz, $Me_6$), 9.2 (q, $^1J_{CH}$ = 128.8 Hz, $C_5\underline{Me}_5$); $^1$H-$^{13}$C HETCORR (100 MHz, $CD_2Cl_2$) δ 98.0 ($C_4$) ↔ δ 4.91 ($H_4$); δ 87.0 ($C_1$) ↔ δ 3.78 ($H_1$); 59.4 ($C_7$) ↔ δ 2.56 ($H_{7exo}$), δ 41.0 ($C_6$) ↔ δ -0.12 ($H_{6endo}$); δ 23.1 (Me) ↔ δ 1.38 (Me); δ 22.6 ($Me_7$) ↔ δ 0.89 ($Me_7$); δ 21.2 (Me) ↔ δ 1.82 (Me); δ 18.6 (Me) ↔ δ 2.21 (Me); δ 15.7 ($Me_6$) ↔ δ 0.85 ($Me_6$); δ 9.2 ($C_5\underline{Me}_5$) ↔ δ 1.66 ($C_5\underline{Me}_5$). Analysis calculated for $C_{23}H_{34}CoF_3O_3S$: C, 54.54; H, 6.77; found: C, 54.357; H, 6.522.

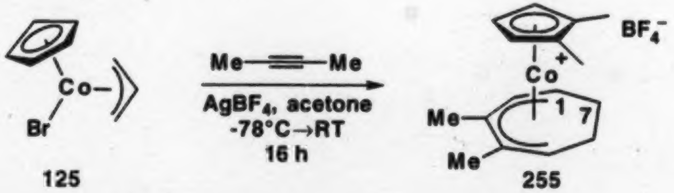
**[($C_5Me_5$)Co($\eta^5$-2,3,5,6-$Me_4$-7-$CH_2D$-$C_7H_4$)]$^+$ OTf$^-$ (252-d$_1$)** This compound was prepared by deuteration of Cp*Co(butadiene) (**82**) with DOTf in diethyl ether at -78°C in $CH_2Cl_2$. The solvent was removed using a canula and the crude product was redissolved in 2,2,2-trifluoroethanol. Excess butyne was added and the solution was heated to 60°C for 12h. Removal of the solvent and precipitation from $CH_2Cl_2$ with diethyl ether provided crude **252**-d$_1$. The $^1$H NMR spectrum is similar to **252** above except for 0.87 (m, $CH_2D$).

**2,3-$^{13}$C-2-Butyne.** A clean, oven-dried Schlenk flask was charged with 16.8 mL of BuLi (2.5 M, hexanes). This solution was reduced *in vacuo* to a thick syrup. The flask was cooled (about 263K), and 25 mL of freshly distilled diethyl ether was added, then the flask was connected to an ampoule containing 0.5 L (approx 21 mmol) $^{13}$C labelled acetylene (CIL, >98% isotopic purity). The flask was cooled to -78 °C, evacuated, and the ampoule was cracked open. A white suspension of $Li_2C_2$ quickly formed. The flask was held at -78 °C for 5 min, then the cooling bath was removed. This suspension was stirred for 1 h, after which the volatiles were all removed *in vacuo*. If so desired, the insoluble dilithioacetylide could be washed free of excess BuLi with pentane. However, the precipitate is so fine that this is difficult, and losses occur.

The solid dilithioacetylide was cooled in a dioxane-dry ice slush (11 °C) and HMPA (30 mL) was added with stirring. CAUTION: Remaining BuLi can react with HMPA at temperatures slightly above room temperature and produce a tarry material which interferes with the reaction. Dimethyl sulfate (42 mmol, 4.2 mL) was then added slowly, with stirring. Once all the dimethyl sulfate had been added, the slurry was stirred 30 min in the cooling bath. The solution was frozen (-196 °C), and the vacuum transfer apparatus was attached. After degassing, the reaction mixture was allowed to warm to room temperature. All volatiles were vacuum transferred to a cooled (-196 °C) flask. 0.91g of a colorless liquid was obtained. $^1$H NMR spectroscopic analysis of purity (pentane impurity) indicated a yield of about 50% overall. $^1$H NMR (300 MHz, $CD_2Cl_2$) $\delta$ 1.72 (t, $^2J_{CH} = {}^3J_{CH} = 3.0$ Hz) ; $^{13}$C NMR (100 MHz, $CD_2Cl_2$) $\delta$ 74.6 (s, $C_2$). The methyl (unlabelled) carbon was not located above baseline noise. Low Resolution MS *m/z* calculated for $^{13}C_2{}^{12}C_2H_6$ ($M^+$): 56.05; found: 56.1 (100%).

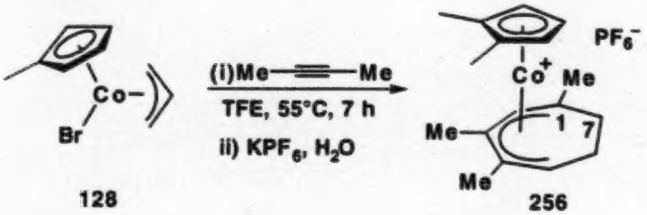


**[$(C_5Me_5)Co(\eta^5$-2,3,5,6-$Me_4$-2,3,5,6-$^{13}C$-$C_7H_5)]^+$ $OTf^-$ (87-$^{13}C_4$).** In the drybox, $[(C_5Me_5)Co(\eta^3$-$C_3H_5)]^+OTf^-$ (**80**) (30.1 mg, 78 μmol) was placed in a glass bomb. The bomb was removed to the Schlenk line and dichloromethane-$d_2$ (2 mL) was added. On the high vacuum line, $^{13}C$-labelled 2-butyne (10 equiv, 780 mmol) was added by vacuum transfer. The solution was warmed to -78 °C, and then allowed to warm slowly to room temperature while being stirred overnight. The solvent was evaporated, the residue washed with diethyl ether and then dissolved in dichloromethane and filtered through Celite. Evaporation gave a red, impure solid (26 mg, 67%). $^1H$ NMR data was complicated by $^2J_{CH}$ and $^3J_{CH}$, which broadened all signals into multiplets. $^{13}C$ NMR (labelled C only, 125 MHz, acetone-$d_6$) δ 119.57 (d, $^1J_{CC}$ = 39.3 Hz, $C_5$), $^a$106.76 (d, $^1J_{CC}$ = 46.3 Hz, $C_{2/3}$), $^a$106.36 (d, $^1J_{CC}$ = 46.3 Hz, $C_{2/3}$), 38.32 (dd, $^1J_{CH}$ = 127.1 Hz, $^1J_{CC}$ = 39.3 Hz, $C_6$). $^a$These carbons lean together in a second order pattern. $^1J_{CH}$ value obtained from gated spectrum run at 100 MHz, acetone-$d_6$. This spectrum also tentatively identified the $C_5\underline{Me_5}$ signal at δ 8.7, $^1J_{CH}$ = 128.3 Hz. The chemical shifts are consistent with the unlabelled material.



**[$(1,2$-$Me_2.C_5H_3)Co(\eta^5$-3,4-$Me_2C_7H_7)]^+$ $BF_4^-$ (255).** In the drybox, $(C_5H_5)Co(\eta^3C_3H_5)(Br)$ (**125**) (0.6129 g, 2.501 mmol) was weighed into a Schlenk flask and removed to the Schlenk line, where acetone (20 mL) was added. The flask was then freeze-pump-thaw degassed three times using the high vacuum line and 2-butyne (12.5 mmol, 5 equiv) was added by vacuum transfer. The solution was allowed to warm to -78°C in a dry-ice acetone bath. Under a nitrogen purge, solid silver tetrafluoroborate (0.535 g, 1.1 equiv) was added. The solution was slowly allowed to warm, with stirring, to room temperature. Purification was effected by flash chromatography on silica gel, using 5% methanol/dichloromethane. A light red-orange band was collected and this was recrystallized several times from dichloromethane/diethyl ether to give a light orange powder (52.9 mg, 6%). IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3110 (m), 2925 (w), 1695 (w), 1477 (m), 1417 (m), 1384 (m), 1269 (s), 1224 (m), 1151 (s), 1060 (s), 1031 (s), 865 (m), 753 (w), 638 (s), 572 (m); $^1H$ NMR (400 MHz, acetone-$d_6$) δ 5.64 (br s, 1H, $C_5\underline{H}_3Me_2$), 5.33 (t, $J$ = 2.6 Hz, 1H, $C_5\underline{H}_3Me_2$), 5.22 (d, $J_{2\text{-}1}$ = 9.4 Hz, 1H, $H_2$), 5.16 (br s, 1H, $C_5\underline{H}_3Me_2$), 5.07-5.00 (m, 2H, $H_{1,5}$), 2.85-2.70 (m, 1H, $H_{7endo}$), 2.54 (s, 3H, $Me_3$), 2.31 (s, 3H, $Me_4$), 2.01 (s, 3H, $C_5H_3\underline{Me}_2$), 1.95 (s, 3H, $C_5H_3\underline{Me}_2$), 2.0-1.9 (m, 1H, $H_{6endo}$, overlaps with Me), 1.75 (br d, $J$ = 16 Hz, 1H, $H_{7exo}$), 0.55-0.45 (m, 1H, $H_{6exo}$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.31 (s, 1H, $C_5\underline{H}_3Me_2$), 5.20 (s, 1H, $C_5\underline{H}_3Me_2$), 5.13 (d, 1H, $H_2$), 5.08 (s, 1H, $C_5\underline{H}_3Me_2$), 5.00-4.95 (m, 1H, $H_1$), 4.85 (dd, $H_5$), 2.75-2.60 (m, 1H, $H_{7endo}$), 2.48 (s, 3H, $Me_3$), 2.24 (s, 3H, $Me_4$), 1.94 (s, 3H, $C_5H_3\underline{Me}_2$), 1.90 (s, 3H, $C_5H_3\underline{Me}_2$), 1.75 (br d, 1H, $H_{7endo}$), 1.60 (m, 1H, $H_{6exo}$), 0.50 (m, 1H, $H_{6endo}$); $^1H$-$^1H$ COSY (400 MHz, acetone-$d_6$) δ 5.64 ($C_5\underline{H}_3Me_2$) ↔ δ 5.33 ($C_5\underline{H}_3Me_2$), δ 5.16 ($C_5\underline{H}_3Me_2$), δ 2.01 (w, $C_5H_3\underline{Me}_2$), δ 1.95 (w, $C_5H_3\underline{Me}_2$); δ 5.33 ($C_5\underline{H}_3Me_2$) ↔ δ 5.16 ($C_5\underline{H}_3Me_2$), δ 2.01 (w, $C_5H_3\underline{Me}_2$), δ 1.95 (w, $C_5H_3\underline{Me}_2$); δ 5.22 ($H_2$) ↔ δ 5.03 ($H_{1/5}$); δ 5.07 ($H_{1/5}$) ↔ δ 2.77 ($H_{7endo}$), δ 1.95 ($H_{6endo}$), δ 1.75 ($H_{7exo}$), δ 0.50 ($H_{6exo}$); δ 2.77 ($H_{7endo}$) ↔ δ 1.95 ($H_{6endo}$), δ 1.75 ($H_{7exo}$); δ 1.95 ($H_{6endo}$) ↔ δ 1.75 ($H_{7exo}$), δ 0.50 ($H_{6exo}$); δ 1.75 ($H_{6endo}$) ↔ δ 0.50 ($H_{6exo}$); $^{13}C$ NMR (100 MHz, acetone-$d_6$) δ 115.5 (s), 109.1 (s), 102.9 (s), 102.6 (s), 96.0 (d, $^1J_{CH}$ = 163.9 Hz, $C_2$), 90.6 (d, $^1J_{CH}$ = 154.5 Hz, $C_1$), 88.4 (dd, $^1J_{CH}$ = 181.3 Hz, $^2J_{CH}$ = 5Hz, $\underline{C}_5H_3Me_2$), 87.3 (d, $^1J_{CH}$ = 182.2 Hz, $\underline{C}_5H_3Me_2$), 86.2 (d, $^1J_{CH}$ = 159.2 Hz,

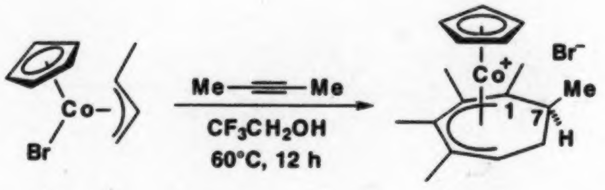
$C_5$), 85.2 (dt, $^1J_{CH}$ = 183.3 Hz, $^2J_{CH}$ = 6Hz, $\underline{C}_5H_3Me_2$), 38.6 (t, $^1J_{CH}$ = 131.7 Hz, $C_7$), 28.1$^a$ (t, $^1J_{CH}$ = 130.2Hz, $C_6$), 21.8 (qd, $^1J_{CH}$ = 128.8 Hz, $^3J_{CH}$ = 5 Hz, $Me_4$), 19.9 (qd, $^1J_{CH}$ = 129.6 Hz, $^3J_{CH}$ = 5Hz, $Me_3$), 10.6 (q, $^1J_{CH}$ = 128.9Hz, $C_5H_3\underline{Me}_2$), 10.2 (q, $^1J_{CH}$ = 128.9Hz, $C_5H_3\underline{Me}_2$). $^a$ Overlaps with solvent peaks. $^1$H-$^{13}$C HETCORR (100 MHz, acetone-$d_6$) δ 96.0 ($C_2$) ↔ δ 5.22 ($H_2$); δ 90.6 ($C_1$) ↔ δ 5.1 ($H_1$); δ 88.4 ($C_5H_3Me_2$) ↔ δ 5.16 ($C_5H_3Me_2$); δ 87.3 ($C_5H_3Me_2$) ↔ δ 5.64 ($C_5H_3Me_2$); δ 86.2 ($C_5$) ↔ δ 5.0 ($H_5$); δ 85.2 ($C_5H_3Me_2$) ↔ δ 5.33 ($C_5H_3Me_2$); δ 38.6 ($C_7$) ↔ δ 2.75 ($H_{7endo}$), δ 1.75 ($H_{7exo}$); δ 28.1 ($C_6$) ↔ δ 1.90 ($H_{6endo}$), δ 0.49 ($H_{6exo}$); δ 21.8 ($Me_4$) ↔ δ 2.31 ($Me_4$); δ 19.9 ($Me_3$) ↔ δ 2.54 ($Me_3$); δ 10.6 ($C_5H_3Me_2$) ↔ δ 2.01 ($C_5H_3Me_2$); δ 10.2 ($C_5H_3Me_2$) ↔ δ 1.95 ($C_5H_3Me_2$). Electrospray MS *m/z* calculated for $C_{16}H_{22}Co$ ($M^+ - BF_4$): 273.105349; found: 273.104998 (100%).



**[($C_5H_3Me_2$)Co(1,3,4-$Me_3C_7H_6$)]$^+$ $PF_6^-$ (256).** To a Kontes flask was added (1-Me-$C_5H_4$)Co($C_3H_4$)Br (**128**) (65.8 mg, 0.254 mmol), followed by 2,2,2-trifluoroethanol (6 mL) and 2-butyne (0.20 mL, 10 equiv). The Kontes valve was closed and the solution was heated to 65 °C in an oil bath for 7h. The flask was cooled and all volatile material was removed *in vacuo*. The residue was extracted into water and the solution was filtered to remove insoluble material. The product was precipitated by the addition of a $NH_4PF_6$ solution and collected by filtration. A light orange powder (46.8 mg, 43%) was obtained. IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3112 (br, w), 2882 (br, w), 1474 (m), 1455 (m), 1382 (m), 1349 (w), 1266 (m), 1117 (w), 1027 (m), 836 (s), 739 (m), 703 (m); $^1$H NMR (300 MHz, $CD_2Cl_2$) δ 5.29 (t, $J$ = 2.7 Hz, 1H, $C_5\underline{H}_3Me_2$), 5.14 (br s, 2H, $C_5\underline{H}_3Me_2$ and $H_2$), 4.73 (t, $J$ = 2.2 Hz, 1H, $C_5\underline{H}_3Me_2$), 4.59 (dd, $J_{5\text{-}6endo}$ = 6.6 Hz, $J_{5\text{-}6exo}$ = 4.0 Hz, 1H, $H_5$), 2.41

(s, 3H, $\mathrm{Me_3}$), 2.40-2.25 (m, 2H, $\mathrm{H_{7exo}}$ and $\mathrm{H_{6exo}}$), 2.09 (s, 3H, $\mathrm{Me_4}$), 1.89 (s, 3H, $\mathrm{C_5H_3\underline{Me_2}}$), 1.83 (s, 3H, $\mathrm{Me_1}$), 1.67 (s, 3H, $\mathrm{C_5H_3\underline{Me_2}}$), 1.37 (m, ddd by decoupling, $J_{\mathrm{7exo\text{-}7endo}}$ = 15.1 Hz, $J_{\mathrm{7exo\text{-}6exo}} = J_{\mathrm{7exo\text{-}6endo}}$ = 5.2 Hz, 1H, $\mathrm{H_{7exo}}$), 0.92 (m, dddd by decoupling, $J_{\mathrm{6exo\text{-}6endo}}$ = 14.3 Hz, $J_{\mathrm{6exo\text{-}7exo}} = J_{\mathrm{6exo\text{-}7endo}}$ = 6.4 Hz, $J_{\mathrm{6exo\text{-}5}}$ = 4.1 Hz, 1H, $\mathrm{H_{6exo}}$); $^1$H-$^1$H GCOSY (300 MHz, $\mathrm{CD_2Cl_2}$) δ 5.29 ($\mathrm{C_5\underline{H}_3Me_2}$) ↔ δ 5.14 ($\mathrm{C_5\underline{H}_3Me_2}$), δ 4.73 ($\mathrm{C_5\underline{H}_3Me_2}$); δ 5.14$^{a}$ ($\mathrm{C_5\underline{H}_3Me_2}$ and $\mathrm{H_2}$) ↔ δ 4.73 ($\mathrm{C_5\underline{H}_3Me_2}$), δ 1.37 (w, $\mathrm{H_7}$); δ 4.59 ($\mathrm{H_5}$) ↔ δ 2.33 ($\mathrm{H_{6endo}}$), δ 0.92 ($\mathrm{H_{6exo}}$); δ 2.33 ($\mathrm{H_{6endo,7endo}}$) ↔ δ 1.37 ($\mathrm{H_{7exo}}$), δ 0.92 ($\mathrm{H_{6exo}}$); 1.37 ($\mathrm{H_{7exo}}$) ↔ δ 0.92 ($\mathrm{H_{6exo}}$). $^{a}$ This signal shows correlations to all 5 methyl groups through 4 or 5 bond coupling. $^{13}$C NMR (100 MHz, $\mathrm{CD_2Cl_2}$) δ 110.8 (s, $\mathrm{C_1}$), 110.3 (s, $\mathrm{C_3}$), 107.7 (s, $\mathrm{C_4}$), 101.3 (s, $\mathrm{\underline{C}_5H_3Me_2}$ quaternary), 101.0 (s, $\mathrm{\underline{C}_5H_3Me_2}$ quaternary), 94.9 (d, $^1J_{\mathrm{CH}}$ = 165.4 Hz, $\mathrm{C_2}$), 88.72$^{a}$ (d, $^1J_{\mathrm{CH}}$ = 180.6 Hz, $\mathrm{\underline{C}_5H_3Me_2}$), 88.67$^{a}$ (d, $^1J_{\mathrm{CH}}$ = 180.6 Hz, $\mathrm{\underline{C}_5H_3Me_2}$), 85.7 (d, $^1J_{\mathrm{CH}}$ = 182.8 Hz, $\mathrm{\underline{C}_5H_3Me_2}$), 83.5 (d, $^1J_{\mathrm{CH}}$ = 151.8Hz, $\mathrm{C_5}$), 40.7 (t, $^1J_{\mathrm{CH}}$ = 132.7 Hz, $\mathrm{C_7}$), 31.4 (t, $^1J_{\mathrm{CH}}$ = 129.5 Hz, $\mathrm{C_6}$), 31.0 (q, $^1J_{\mathrm{CH}}$ = 127.6 Hz, $\mathrm{Me_1}$), 21.5 (q, $^1J_{\mathrm{CH}}$ = 129.0 Hz, $\mathrm{Me_4}$), 20.3 (q, $^1J_{\mathrm{CH}}$ = 129.0 Hz, $\mathrm{Me_3}$), 10.5 (q, $^1J_{\mathrm{CH}}$ = 129.2 Hz, $\mathrm{C_5H_3\underline{Me_2}}$), 10.3 (q, $^1J_{\mathrm{CH}}$ = 129.2 Hz, $\mathrm{C_5H_3\underline{Me_2}}$). $^{a}$These signals overlap in the gated decoupled spectrum. HMQC (300 MHz, $\mathrm{CD_2Cl_2}$) δ 94.9 ($\mathrm{C_2}$) ↔ δ 5.14 ($\mathrm{H_2}$); δ 88.72 ($\mathrm{\underline{C}_5H_3Me_2}$) ↔ δ 4.73 ($\mathrm{C_5\underline{H}_3Me_2}$); δ 88.67 ($\mathrm{\underline{C}_5H_3Me_2}$) ↔ δ 5.14 ($\mathrm{C_5\underline{H}_3Me_2}$); δ 85.7 ($\mathrm{\underline{C}_5H_3Me_2}$) ↔ δ 5.29 ($\mathrm{C_5\underline{H}_3Me_2}$); δ 83.5 ($\mathrm{C_5}$) ↔ δ 4.59 ($\mathrm{H_5}$); δ 40.7 ($\mathrm{C_7}$) ↔ δ 2.33 ($\mathrm{H_{7endo}}$), δ 1.37 ($\mathrm{H_{7exo}}$); δ 31.4 ($\mathrm{C_6}$) ↔ δ 2.33 ($\mathrm{H_{6endo}}$), δ 0.92 ($\mathrm{H_{6exo}}$); δ 31.0 ($\mathrm{Me_1}$) ↔ δ 1.83 ($\mathrm{Me_1}$); δ 21.5 ($\mathrm{Me_4}$) ↔ δ 2.09 ($\mathrm{Me_4}$); δ 20.3 ($\mathrm{Me_3}$) ↔ δ 2.41 ($\mathrm{Me_3}$); δ 10.5 ($\mathrm{C_5H_3\underline{Me_2}}$) ↔ δ 1.89 ($\mathrm{C_5H_3\underline{Me_2}}$); δ 10.3 ($\mathrm{C_5H_3\underline{Me_2}}$) ↔ δ 1.67 ($\mathrm{C_5H_3\underline{Me_2}}$); HMBC (300 MHz, $\mathrm{CD_2Cl_2}$) δ 110.8 ($\mathrm{C_1}$) ↔ δ 2.33 ($\mathrm{H_{6endo,7endo}}$), δ 1.83 ($\mathrm{Me_1}$), δ 1.37 ($\mathrm{H_{7exo}}$), δ 0.92 ($\mathrm{H_{6exo}}$); δ 110.3 ($\mathrm{C_3}$) ↔ δ 4.59 ($\mathrm{H_5}$), δ 2.41 ($\mathrm{Me_3}$), δ 2.09 ($\mathrm{Me_4}$); δ 107.7 ($\mathrm{C_4}$) ↔ δ 5.14 ($\mathrm{H_2}$), δ 2.41 ($\mathrm{Me_3}$), δ 2.09 ($\mathrm{Me_4}$), δ 2.33 ($\mathrm{H_{6endo,7endo}}$), δ 0.92 ($\mathrm{H_{6exo}}$); δ 101.3/101.0$^{a}$ ($\mathrm{\underline{C}_5H_3Me_2}$ ring quaternaries) ↔ δ 5.29 ($\mathrm{C_5\underline{H}_3Me_2}$), δ 5.14 ($\mathrm{C_5\underline{H}_3Me_2}$), δ 4.73 ($\mathrm{C_5\underline{H}_3Me_2}$), δ 1.89 ($\mathrm{C_5H_3\underline{Me_2}}$), δ 1.67 ($\mathrm{C_5H_3\underline{Me_2}}$); δ 94.9 ($\mathrm{C_2}$) ↔ δ 2.41 ($\mathrm{Me_3}$), δ 2.33 ($\mathrm{H_{6endo,7endo}}$), δ 1.83 ($\mathrm{Me_1}$), δ 1.37

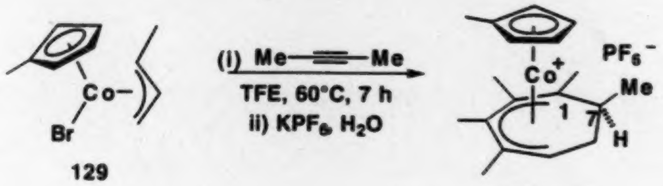
($H_{7exo}$); δ 88.72/88.67$^a$ ($\underline{C}_5H_3Me_2$) ↔ δ 5.29 ($C_5\underline{H}_3Me_2$), δ 5.14 ($C_5\underline{H}_3Me_2$), δ 4.73 ($C_5\underline{H}_3Me_2$), δ 1.89 ($C_5H_3\underline{Me}_2$), δ 1.67 ($C_5H_3\underline{Me}_2$); δ 85.7 ($\underline{C}_5H_3Me_2$) ↔ δ 5.29 ($C_5\underline{H}_3Me_2$), δ 5.14 ($C_5\underline{H}_3Me_2$), δ 4.73 ($C_5\underline{H}_3Me_2$); δ 83.5 ($C_5$) ↔ δ 2.33 ($H_{6endo,7endo}$), δ 2.09 ($Me_4$), δ 1.37 ($H_{7exo}$), δ 0.92 ($H_{6exo}$); δ 31$^b$ ↔ δ 5.14 ($H_2$), δ 4.59 ($H_5$), δ 2.33 ($H_{6endo,7endo}$), δ 1.37 ($H_{7exo}$); δ 21.5 ($Me_4$) ↔ δ 4.59 ($H_5$); δ 20.3 ($Me_3$) ↔ δ 5.14 ($H_2$). $^a$ These signals are not resolved in the spectrum. $^b$Two signals overlap: δ 31.4 ($C_6$) and δ 31.0 ($Me_1$). Analysis calculated for $C_{17}H_{24}CoF_6P$: C, 47.23; H, 5.59; found: C, 46.671; H, 5.392. Electrospray MS *m/z* calculated for $C_{17}H_{24}Co$ ($M^+$ - $PF_6$): 287.120999; found: 287.120454 (100%).



126 257

**[($C_5H_5$)Co(1,2,3,4,7-$Me_5C_7H_4$)]$^+$ Br$^-$ (257).** To a Kontes flask was added ($C_5H_5$)Co(1-Me-$C_3H_4$) (Br) (**126**) (85.2 mg, 0.329 mmol) and 2,2,2-trifluoroethanol (3 mL). The solution was freeze-pump-thaw degassed and 2-butyne (10 equiv) was added by vacuum transfer. The flask was heated in an oil bath maintained at 60 °C for 12 h. All volatile material was removed *in vacuo* and the residue was purified by flash chromatography using 5% methanol/dichloromethane on silica gel. An orange powder (65 mg, 54%) was obtained. IR ($CH_2Cl_2$ cast, cm$^1$) 3038 (s), 2961 (s), 2924 (s), 2871 (s), 2833 (m), 2736 (w), 1618 (w), 1452 (s), 1428 (s), 1410 (s), 1389 (s), 1380 (s), 1345 (m), 1275 (w), 1243 (w), 1100 (w), 1077 (m), 1053 (m), 1014 (s), 999 (m), 935 (w), 865 (s), 832 (w), 730 (s), 696 (m), 653 (w), 597 (w), 498 (w); $^1$H NMR (300 MHz, $CDCl_3$) δ 5.35 (s, 5H, $C_5\underline{H}_5$), 5.35 (m, 1H, $H_5$), 2.72 (ddd, $J_{6endo\text{-}6exo}$ = 15.2 Hz, $J_{6endo\text{-}7}$ = 9.1 Hz, $J_{6endo\text{-}5}$ = 5.8 Hz, 1H, $H_{6endo}$), 2.57 (s, 3H, Me), 2.57 (m, 1H, $H_7$), 2.30 (s, 3H, Me), 2.28 (s, 3H, Me), 1.92 (s, 3H, Me), 0.99 (dt, $J_{6exo\text{-}6endo}$ = 15.7 Hz, $J_{6exo\text{-}5}$ = $J_{6exo\text{-}7}$ = 3.6 Hz, 1H, $H_{6exo}$), 0.38 (d, $J_{Me\text{-}7}$ = 6.9 Hz, 3H,

$Me_7$); $^1H$-$^1H$ COSY (400 MHz, $CD_2Cl_2$) δ 5.35 ($H_5$) ↔ δ 2.72 ($H_{6endo}$), δ 0.99 (w, $H_{6exo}$); δ 2.72 ($H_{6endo}$) ↔ δ 0.99 (w, $H_{6exo}$); δ 2.57 ($H_7$) ↔ δ 0.99 ($H_{6exo}$), δ 0.38 ($Me_7$); $^{13}C$ NMR (100 MHz, $CD_2Cl_2$) δ 115.2 (s, $C_3$), 106.7 (s, $C_{1/2/4}$), 105.1 (s, $C_{1/2/4}$), 103.7 (s, $C_{1/2/4}$), 89.7 (d, $^1J_{CH}$ = 181.5 Hz, $C_5H_5$), 81.7 (d, $^1J_{CH}$ = 158.6 Hz, $C_5$), 46.7 (d, $^1J_{CH}$ = 134.4 Hz, $C_7$), 42.2 (t, $^1J_{CH}$ = 128.4 Hz, $C_6$), 31.8 (q, $^1J_{CH}$ = 127.8 Hz, Me), 27.0 (q, $^1J_{CH}$ = 128.0 Hz, Me), 21.4 (q, $^1J_{CH}$ = 129.1 Hz, Me), 21.1 (q, $^1J_{CH}$ = 125.8 Hz, Me), 20.4 (q, $^1J_{CH}$ = 129.2 Hz, $Me_7$); $^1H$-$^{13}C$ HETCORR (100 MHz, $CD_2Cl_2$) δ 89.7 ($\underline{C}_5H_5$) ↔ δ 5.35 ($C_5\underline{H}_5$); δ 81.7 ($C_5$) ↔ δ 5.35 ($H_5$); δ 46.7 ($C_7$) ↔ δ 2.57 ($H_7$); δ 42.2 ($C_6$) ↔ δ 2.72 ($H_{6endo}$), 0.99 ($H_{6exo}$); δ 31.8 (Me) ↔ δ 1.92 (Me); δ 27.0 (Me) ↔ δ 2.28 (Me); δ 21.4 (Me) ↔ δ 2.30 (Me); δ 21.1 (Me) ↔ δ 2.57 (Me); δ 20.4 ($Me_7$) ↔ δ 0.38 ($Me_7$). Analysis calculated for $C_{17}H_{24}CoBr$: C, 55.60; H, 6.59; found: C, 55.382; H, 6.440.

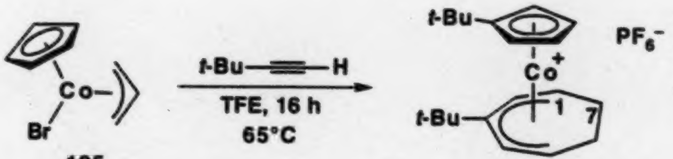


129

258

**[($C_5H_4Me$)Co(1,2,3,4,7-$Me_5C_7H_4$)]$^+$ $Br^-$ (258).** To a Kontes flask was added (1-Me-$C_5H_4$)Co(1-Me-$C_3H_4$)Br (**129**) (85 mg, 0.31 mmol), followed by 2,2,2-trifluoroethanol (5 mL) and 2-butyne (0.24 mL, 10 equiv). The flask was sealed and heated to 60 °C in an oil bath for 7 h. The flask was cooled and all volatile material was removed *in vacuo*. The residue was extracted into water (3 mL), filtered and the product precipitated by addition of a solution of $NH_4PF_6$. The solid was collected and purified further by flash chromatography on silica gel, using 5% methanol/dichloromethane as the eluent. A orange-red solid (55 mg, 39%) was obtained. IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3116 (w), 2972 (w), 2931 (w), 1456 (m), 1381 (m), 1031 (w), 838 (s), 740 (w), 557 (m); $^1H$ NMR (300 MHz, $CDCl_3$) δ 5.53 (br s, 1H, $C_5\underline{H}_4Me$), 5.37 (br s, 1H, $C_5\underline{H}_4Me$), 5.13 (br s, 1H, $C_5\underline{H}_4Me$), 5.08 (dd, $J_{5\text{-}6endo}$ = 5.4 Hz, $J_{5\text{-}6exo}$ = 3.6 Hz, 1H, $H_5$), 4.83 (br s, 1H,

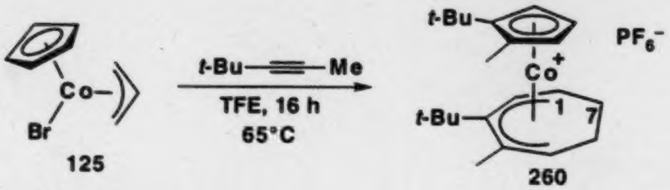
$C_5\underline{H}_4Me$), 2.84 (ddd, $J_{6endo\text{-}6exo}$ = 15.3 Hz, $J_{6endo\text{-}7}$ = 9.3 Hz, $J_{6endo\text{-}5}$ = 5.7 Hz, 1H, $H_{6endo}$), 2.6-2.5 (m, 1H, obscured by Me, 1H, $H_7$), 2.52 (s, 3H, Me), 2.28 (s, 6H, 2 Me), 2.05 (s, 3H, Me), 1.93 (s, 3H, Me), 1.14 (dt, $J_{6exo\text{-}6endo}$ = 15.9 Hz, $J_{6exo\text{-}5} = J_{6exo\text{-}7}$ = 3.9 Hz, 1H, $H_{6exo}$), 0.39 (d, $J$ = 7.2 Hz, 3H, $Me_7$); $^1H$-$^1H$ GCOSY (300 MHz, $CDCl_3$) δ 5.53 ($C_5\underline{H}_4Me$) ↔ δ 5.37 ($C_5\underline{H}_4Me$), δ 5.13 ($C_5\underline{H}_4Me$), δ 4.83 ($C_5\underline{H}_4Me$); δ 5.37 ($C_5\underline{H}_4Me$) ↔ δ 5.13 ($C_5\underline{H}_4Me$), δ 4.83 ($C_5\underline{H}_4Me$); δ 5.13 ($C_5\underline{H}_4Me$) ↔ δ 4.83 ($C_5\underline{H}_4Me$); δ 5.08 ($H_5$) ↔ δ 2.84 ($H_{6endo}$), δ 1.14 ($H_{6exo}$); δ 2.84 ($H_{6endo}$) ↔ 2.55 ($H_7$), δ 1.14 ($H_{6exo}$); δ 2.55 ($H_7$) ↔ δ 1.14 ($H_{6exo}$), δ 0.39 ($Me_7$); $^{13}C$ NMR[a] (75 MHz, $CDCl_3$) δ 131.8 (s, $C_3$), 105.7 (s, $C_{1,2,4}$), 105.3 (s, $C_{1,2,4}$), 89.7 (d, $^1J_{CH}$ = 186 Hz, $\underline{C}_5H_4Me$), 89.2 (d, $^1J_{CH}$ = 184 Hz, $\underline{C}_5H_4Me$), 89.2[b] (d, $^1J_{CH}$ = 181 Hz, $\underline{C}_5H_4Me$), 88.7 (d, $^1J_{CH}$ = 183 Hz, $\underline{C}_5H_4Me$), 82.6 (d, $^1J_{CH}$ = 154 Hz, $C_5$), 46.1 (d, $^1J_{CH}$ = 135 Hz, $C_7$), 42.3 (t, $^1J_{CH} \approx$ 135 Hz, $C_6$), 31.1 (q, $^1J_{CH}$ = 130 Hz, Me), 25.5 (q, $^1J_{CH}$ = 130 Hz, Me), 21.3 (q, $^1J_{CH}$ = 130 Hz, $Me_6$), 20.4 (q, $^1J_{CH}$ = 130 Hz, Me), 19.0 (q, $^1J_{CH}$ = 130 Hz, Me), 12.6 (q, $^1J_{CH}$ = 130 Hz, $C_5H_4\underline{Me}$). [a]Values for the $^1J_{CH}$ coupling constant are obtained from the HMQC spectrum. [b]Two Cp' ring carbons overlap. HMQC (300 MHz, $CDCl_3$) δ 89.7 ($\underline{C}_5H_4Me$) ↔ δ 5.37 ($\underline{C}_5H_4Me$); δ 89.2 ($\underline{C}_5H_4Me$) ↔ δ 5.53 ($\underline{C}_5H_4Me$); δ 89.2 ($\underline{C}_5H_4Me$) ↔ δ 4.83 ($\underline{C}_5H_4Me$); δ 88.7 ($\underline{C}_5H_4Me$) ↔ δ 5.13 ($\underline{C}_5H_4Me$); δ 82.6 ($C_1$) ↔ δ 5.08 ($H_5$); δ 46.1 ($C_7$) ↔ δ 2.55 ($H_7$); δ 42.3 ($C_6$) ↔ δ 2.84 ($H_{6endo}$), δ 1.14 ($H_{6exo}$); δ 31.1 (Me) ↔ δ 1.93 (Me); δ 25.5 (Me) ↔ δ 2.28 (Me); δ 21.3 ($Me_7$) ↔ δ 0.39 ($Me_7$); δ 20.4 (Me) ↔ δ 2.28 (Me); δ 19.0 (Me) ↔ δ 2.52 (Me); δ 12.6 ($C_5H_4\underline{Me}$) ↔ δ 2.05 ($C_5H_4\underline{Me}$). Analysis calculated for $C_{18}H_{26}CoF_6P$: C, 48.44; H, 5.87; found: C, 48.232; H, 5.829.



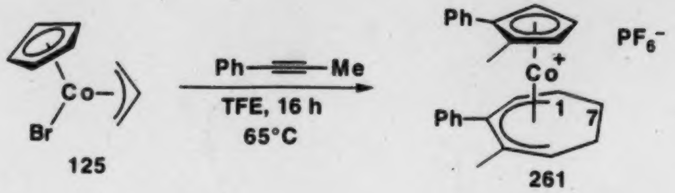
125

259

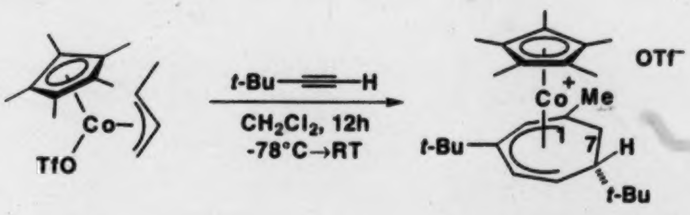
**[(1-*t*-Bu-$C_5H_4$)Co(3-*t*-Bu$C_7H_6$)]$^+$ $PF_6^-$ (259).** To a solution of CpCo($C_3H_5$)(Br) (**125**) (34.9 mg, 0.142 mmol) in trifluoroethanol (5 mL) in a Kontes flask was added *t*-butylacetylene (0.18 mL, 10 equiv). The Kontes valve was then closed and the solution was heated at 65°C for 16 h. The solution was cooled and the solvent was removed *in vacuo*. The residue was extracted into warm water. The extract was filtered and the product was precipitated by the addition of $KPF_6$. The product was extracted into dichloromethane. The dichloromethane layer was dried ($Na_2SO_4$) and the solvent was removed. An orange-red powder (11.3 mg, 17%) was collected. The $^1$H NMR spectrum of this complex is identical to that of the product obtained from the reaction between ($\eta^5$-$C_5H_5$)Co($\eta^4$-1-*t*-Bu$C_5H_5$), $HBF_4$ and *t*-butylacetylene (**331**, *ide infra*).



**[(1-*t*-Bu-2-Me-$C_5H_3$)Co(3-*t*-Bu-4-Me$C_7H_7$)]$^+$ $PF_6^-$ (260).** To a solution of CpCo($C_3H_5$)(Br) (**125**) (53.8 mg, 0.220 mmol) in trifluoroethanol (3 mL) in a Kontes flask was added 4,4-dimethyl-2-pentyne (0.3 mL, 10 equiv). The Kontes valve was then closed and the solution was heated at 65°C for 16 h. The solution was cooled and the solvent was removed *in vacuo*. The residue was extracted into warm water. The extract was filtered and the product was precipitated by the addition of $KPF_6$. The product was extracted into dichloromethane. The dichloromethane layer was dried ($Na_2SO_4$) and the solvent was removed. An orange-red powder (22.7 mg, 21%) was collected. $^1$H NMR (300 MHz, $CDCl_3$) (select data only) δ 5.7-4.6 (series of overlapping signals), 2.9-2.7 (m), 2.38 (s, Me), 2.26 (s, Me), 1.9 (br d, *J* ca. 15 Hz), 1.85-1.65 (m), 1.61 (s, *t*-Bu), 1.47 (s, *t*-Bu), 0.3-0.1 (m). Electrospray MS *m/z* calculated for $C_{22}H_{34}Co$ ($M^+ - PF_6$): 357.199249; found: 357.198996 (100%).



**[(1-Ph-2-Me-$C_5H_3$)Co(3-Ph-4-Me$C_7H_7$)]$^+$ $PF_6^-$ (261).** To a solution of CpCo($C_3H_5$)(Br) (**125**) (30.7 mg, 0.125 mmol) in trifluoroethanol (4 mL) in a Kontes flask was added phenylpropyne (0.076 mL, 5 equiv). The Kontes valve was then closed and the solution was heated at 65°C for 16 h. The solution was cooled and the solvent was removed *in vacuo*. The residue was extracted into warm water. The extract was filtered and the product was precipitated by the addition of $KPF_6$. The product was extracted into dichloromethane. The dichloromethane layer was dried ($Na_2SO_4$) and the solvent was removed. An orange-red impure powder (9.9 mg, 15%) was collected. Impurities prohibited definite assignment of the $^1$NMR spectrum. $^1$H NMR (300 MHz, $CDCl_3$) (select data only) δ 7.50-7.25 (m, $H_{Ph}$), 5.9-4.9 (series of overlapping signals), 3.0-2.8 (m), 0.6-0.4 (m). Methyl signals could not be conclusively assigned. Electrospray MS *m/z* calculated for $C_{26}H_{26}Co$ ($M^+$ - $PF_6$): 397.136649; found: 397.136070 (100%).

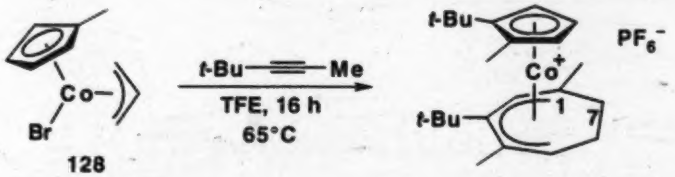


81

262, major isomer

**[($C_5Me_5$)Co(3,6-*t*-$Bu_2$-1-Me-$C_7H_6$)]$^+$ $BF_4^-$ (262).** A Schlenk flask was charged with ($C_5Me_5$)Co(1-Me-$C_3H_4$)(OTf) (**81**) (58.6 mg, 0.147 mmol). The solid was dissolved in dichloromethane (10 mL) and cooled to -78°C. 3,3-Dimethyl-1-butyne (0.27 mL, 15 equiv) was added and the solution was allowed to warm to room temperature overnight.

The solvent was removed and the residue was purified by column chromatography (silica gel, 5% methanol/dichloromethane). A red fraction was collected and dried to give an orange-red solid (27 mg, 33%), which appeared to contain at least two complexes by $^1$H NMR spectroscopy. However, the title compound was identified as the major isomer. $^1$H NMR (400 MHz, $CDCl_3$) δ 5.01 (d, $J_{4\text{-}5}$ = 8.2 Hz, 1H, $H_4$), 4.63 (s, 1H, $H_2$), 4.01 (dd, $J_{5\text{-}4}$ = 8.0 Hz, $J_{5\text{-}6endo}$ = 5.3 Hz, 1H, $H_5$), 2.53 (dd, $J_{7endo\text{-}7exo}$ = 17.2 Hz, $J_{7endo\text{-}6endo}$ = 12.1 Hz, 1H, $H_{7endo}$), 2.05-1.95 (m, obscured by impurities, 1H, $H_{7exo}$), 1.88 (s, 3H, Me), 1.75 (s, 15H, $C_5Me_5$), 1.48 (s, 9H, *t*-Bu), 0.82 (s, 9H, *t*-Bu), -0.16 (ddd, $J_{6endo\text{-}7endo}$ = 12.1 Hz, $J_{6endo\text{-}7exo}$ = $J_{6endo\text{-}5}$ = 5.0 Hz, 1H, $H_{6endo}$); $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) δ 5.09 ($H_4$) ↔ δ 4.01 ($H_5$); δ 4.01 ($H_5$) ↔ δ -0.16 ($H_{6endo}$); δ 2.53 ($H_{7endo}$) ↔ δ 2.00 ($H_{7exo}$), δ -0.16 ($H_{6endo}$); δ 2.00 ($H_{7exo}$) ↔ δ -0.16 ($H_{6endo}$).



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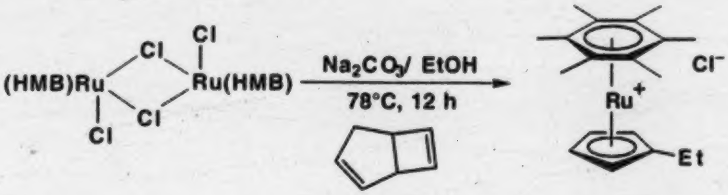
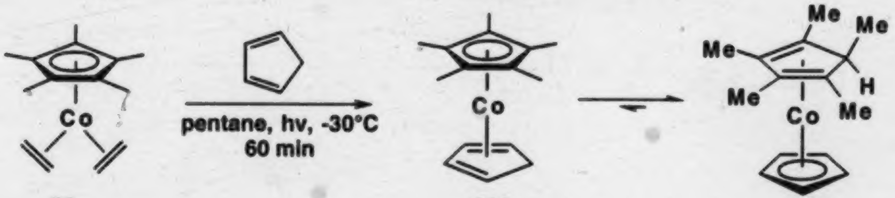
**[(1-*t*-Bu-2-Me-$C_5H_3$)Co(3-*t*-Bu-1,4-$Me_2C_7H_6$)]$^+$ $PF_6^-$(349).** To a solution of (1-Me-$C_5H_4$)Co($C_3H_5$)(Br) **(128)** (22.0 mg, 0.085 mmol) in trifluoroethanol (4 mL) in a Kontes flask was added 4,4-dimethyl-2-pentyne (0.11 mL, 10 equiv). The Kontes valve was then closed and the solution was heated at 65°C for 16 h. The solution was cooled and the solvent was removed *in vacuo*. The residue was extracted into warm water. The extract was filtered and the product was precipitated by the addition of $KPF_6$. The product was then isolated and purified by column chromatography (silica gel, 5% methanol/dichloromethane). An orange powder (14.3 mg, 37%) was obtained, with the title complex identified as the major component by comparison with the $^1$H NMR spectrum of the authentic material (*vide infra*) Electrospray MS *m/z* calculated for $C_{23}H_{36}Co$ ($M^+ - PF_6$): 371.214899; found: 371.214891 (100%). The minor isomer is tentatively identified as the 1,2,3-trisubstituted seven-membered ring based on comparison of the $^1$H NMR spectrum to that of other 1,2,3-trisubstituted cycloheptadienyl complexes (*e.g.* **350**, **355**, *vide infra*).



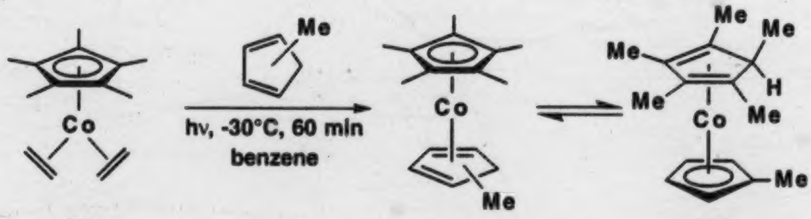
**[$(C_6Me_6)Ru(\eta^5\text{-}Et\text{-}C_5H_4)]^+ Cl^-$**. To a solution of [$(HMB)RuCl_2]_2$ (51.6 mg, 77.1 μmol) in absolute ethanol (10 mL) under nitrogen was added sodium carbonate (0.13 g, excess) and bicyclo[3.2.0]hepta-2,5-diene (100 μL, excess). The red solution was heated to reflux for 24 h, after which the color had faded to yellow-orange. The solution was cooled and the solvent was removed *in vacuo*. In the drybox, the residue was triturated with pentane. Outside the drybox, the residue was extracted with dichloromethane and the extracts were filtered through a short Celite column. The solvent was removed, leaving an off-white powder (21.4 mg, 70%). $^1$H NMR (400 MHz, $CDCl_3$) δ 5.05 (br s, 2H, Cp), 4.91 (br s, 2H, Cp), 2.38 (s, 18H, $C_6\underline{Me_6}$), 2.09 (q, *J* = 7.5 Hz, 2H, $C\underline{H_2}CH_3$), 1.09 (t, *J* = 7.5 Hz, 3H, $CH_2C\underline{H_3}$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 102.4 (Cp), 99.1 ($\underline{C_6}Me_6$), 92.0 (Cp), 80.7 (Cp), 20.0 ($CH_2$), 17.7 ($C_6\underline{Me_6}$), 14.9 ($CH_3$).



79 296 297

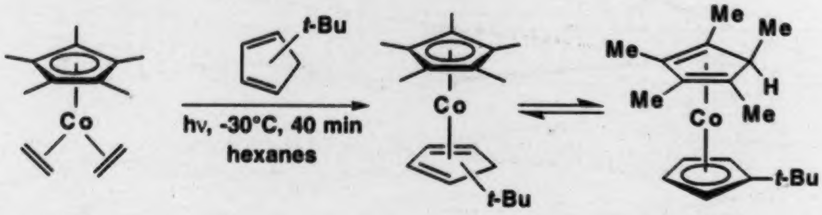
**($\eta^5$-$C_5Me_5$)Co($\eta^4$-$C_5H_6$) (296) and ($\eta^5$-$C_5H_5$)Co($\eta^4$-$C_5Me_5H$) (297)** To a Schlenk tube was added $(C_5Me_5)Co(C_2H_4)_2$ (**79**) (0.2364 g, 0.9446 mmol). Pentane (50 mL) was added, and the tube was removed from the drybox. On the Schlenk line cyclopentadiene (0.45 mL, 5 equiv) was added and the tube was cooled to -30 °C. Photolysis was carried out for 60 min, with a nitrogen purge to remove ethylene. After photolysis, the solvent was removed and the residue extracted with pentane (8 mL) in the drybox. The pentane extract was filtered through a Celite pad and then taken to dryness. A red-orange solid residue (0.2432 g, 99%) was left, consisting of about a 2:1 mixture of $(\eta^5\text{-}C_5Me_5)Co(\eta^4\text{-}C_5H_6)$ (**296**) and $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_5Me_5H)$ (**297**). Depending on photolysis time and other variables, this ratio can change from about 1:3 to 6:1. This mixture was used without further purification or separation. Data for $(C_5H_5)Co(\eta^4\text{-}C_5Me_5H)$ (**297**). IR (hexane cast, $cm^{-1}$) 3093 (w), 3040 (m), 2949 (s), 2907 (s), 2856 (s), 2721 (s), 1652 (m), 1447 (s), 1378 (s), 1334 (m), 1308 (w), 1236 (w), 1107 (w), 1065 (m), 1027 (m), 1006 (m), 990 (m), 795 (s), 402 (s); $^1H$ NMR (300 MHz, $C_6D_6$) $\delta$ 4.36 (s, 5H, $C_5\underline{H_5}$), 2.48 (q, $J$ = 6.0 Hz, 1H, $C_5Me_5\underline{H}$), 2.10 (s, 6H, Me), 1.18 (s, 6H, Me), 0.28 (d, $J$ = 6.1 Hz, 3H, Me); $^{13}C$ NMR (100 MHz, $C_6D_6$) $\delta$ 89.0, 80.8 ($\underline{C}_5H_5$), 56.7, 41.4, 20.4, 15.2, 12.6. MS *m/z* calculated for $C_{15}H_{21}Co$ ($M^+$): 260.09753; found: 260.09757 (96%). MS *m/z* calculated for $C_{15}H_{19}Co$ ($M^+\text{-}H_2$): 258.08188; found: 258.08223(100%).

Data for $(\eta^5\text{-}C_5Me_5)Co(\eta^4\text{-}C_5H_6)$ (**296**): $^1H$ NMR (300 MHz, $C_6D_6$) $\delta$ 4.75 (t, $J$ = 1.9 Hz, 2H, $H_{2,3}$), 2.66 (dt, $J$ = 13.5, 2.2 Hz, 1H, $H_{5a}$), 2.30$^a$ (br d, $J$ = 13.5 Hz, 1H, $H_{5b}$), 1.76 (m, 2H, obscured by $C_5Me_5$, $H_{1,4}$), 1.74 (s, 15H, $C_5\underline{Me_5}$). $^a$This signal apparently has an unreolved triplet of about 1-2 Hz, as determined by the shoulders on the doublet peaks.



79 298 (Eq. 102)

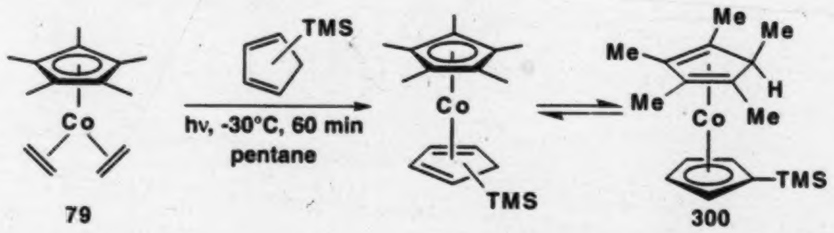
**$(\eta^5\text{-}C_5H_4Me)Co(\eta^4\text{-}C_5Me_5H)$ (298).** To a Schlenk tube was added $(C_5Me_5)Co(C_2H_4)_2$ (**79**) (0.1760 g, 0.7032 mmol). Benzene (50 mL) was added, and the tube was removed from the drybox. On the Schlenk line, methylcyclopentadiene (0.40 mL, 5 equiv) was added and the tube was placed in a cooling bath initially maintained at -30 °C. Photolysis was carried out for 60 min, with a nitrogen purge to remove ethylene. After photolysis, the solvent was removed and the residue extracted with pentane (about 10 mL) in the drybox. The pentane extract was filtered through a Celite pad and then taken to dryness. A red-orange oily residue (0.1744 g, 90%) was obtained, which consisted of a about a 1.6:1 mixture of ($\eta^5$-$C_5H_4Me$)Co($\eta^4$-$C_5Me_5H$) (**298**) and its isomer ($\eta^5$-$C_5Me_5$)Co($\eta^4$-Me-$C_5H_5$). This mixture was used without further purification or separation. Data for ($C_5H_4Me$)Co($\eta^4C_5Me_5H$). IR (hexane cast, $cm^{-1}$) 3035 (m), 2959 (s), 2909 (s), 2704 (m), 1615 (w), 1448 (s), 1374 (m), 1269 (m), 1028 (m), 937 (w), 881 (w), 817 (w), 704 (w); $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 4.19 (t, $J$ = 2 Hz, 2H, Cp'), 4.13 (t, $J$ = 2 Hz, 2H, Cp'), 2.45 (q, $J$ = 6.1 Hz, 1H, $C_5Me_5\underline{H}$), 1.83 (s, 3H, Cp'), 2.02 (s, 6H, Me), 1.17 (s, 6H, Me), 0.45 (d, $J$ = 6.1 Hz, 3H); $^{13}C$ NMR (100 MHz, $C_6D_6$) $\delta$ 92.3 (Cp' quaternary), 88.6, 81.7 (Cp'), 80.3 (Cp'), 56.4, 45.0, 20.2, 14.6, 12.1, 10.3 (Cp' Me). MS *m/z* calculated for $C_{16}H_{23}Co$ ($M^+$): 274.10535 found: 274.11296 (15%). MS *m/z* calculated for $C_{15}H_{20}Co$ ($M^+$-$CH_3$): 259.08969 found: 259.08967 (100%).



79

299

**($\eta^5$-$C_5H_4$*t*-Bu)Co($\eta^4$-$C_5Me_5H$) (299).** To a Schlenk tube was added ($C_5Me_5$)Co($C_2H_4$)$_2$ (**79**) (0.1858 g, 0.7424 mmol). Hexane (40 mL) was added, and the tube was removed from the drybox. On the Schlenk line, *t*-butylcyclopentadiene (0.27 mL, 3 equiv) was added and the tube was initially maintained at -30 °C. Photolysis was carried out for 40 min, with a nitrogen purge to remove ethylene. After photolysis, the solvent was reduced to about 10 mL and filtered through a Celite pad. After the solvent was removed, a red-orange solid residue (0.2326 g, 99%) remained, which consisted of about a 1.3:1 mixture of ($\eta^5$-*t*-Bu$C_5H_4$)Co($\eta^4$-$C_5Me_5H$) (**299**) and its isomer ($\eta^5$-$C_5Me_5$)Co($\eta^4$-*t*-Bu$C_5H_5$). This mixture was used without further purification or separation. Data for ($\eta^5$-*t*-Bu$C_5H_4$)Co($\eta^4$-$C_5Me_5H$). IR (hexane cast, $cm^{-1}$) 3037 (m), 2956 (s), 2902 (s), 2720 (m), 1634 (w), 1457 (m), 1378 (s), 1362 (m), 1273 (w), 1028 (m), 909 (w), 855 (w), 803 (w), 408 (w); $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 4.06 (br s, 2H, $Cp^t$), 3.97 (br s, 2H, $Cp^t$), 2.55 (q, $J$ = 6.0 Hz, 1H, $C_5Me_5\underline{H}$), 1.99 (s, 6H, Me), 1.33 (s, 9H, *t*-Bu), 1.11 (s, 6H, Me), 0.36 (d, $J$ = 6.0 Hz, 3H, Me); $^{13}C$ NMR (100 MHz, $C_6D_6$) $\delta$ 88.5, 80.4 ($Cp^t$), 76.9 ($Cp^t$), 56.7, 43.0, 32.1 (*t*-Bu), 20.4, 14.9, 12.8. $Cp^t$ ring quaternary and *t*-Bu quaternary carbons were not located. MS *m/z* calculated for $C_{19}H_{28}Co$ ($M^+$-H): 315.15231; found: 315.15225 (64%). MS *m/z* calculated for $C_{15}H_{20}Co$ ($M^+$-*t*-Bu): 259.08969; found: 259.08989 (100%).



**($\eta^5$-$C_5H_4SiMe_3$)Co($\eta^4$-$C_5Me_5H$) (300).** To a Schlenk tube was added ($C_5Me_5$)Co($C_2H_4$)$_2$ (**79**) (0.1531 g, 0.6117 mmol). Pentane (50 mL) was added, and the tube was removed from the drybox. On the Schlenk line, (trimethylsilyl)cyclopentadiene (0.36 mL, 3 equiv) was added and the tube was cooled to -30 °C. Photolysis was carried out for 60 min, with a nitrogen purge to remove ethylene. After photolysis, the solvent was removed and the residue extracted with pentane (about 10 mL) in the drybox. The pentane extract was filtered through a Celite pad and then taken to dryness. A red-orange oily residue (0.2120 g, about 100%) was obtained, which consisted of about a 1.6:1 mixture of ($\eta^5$-$SiMe_3$-$C_5H_4$)Co($\eta^4$-$C_5Me_5H$) (**300**) and its isomer ($\eta^5$-$C_5Me_5$)Co($\eta^4$-

$(SiMe_3)C_5H_5$). This mixture was used without further purification or separation. Data for ($\eta^5$-$SiMe_3$-$C_5H_4$)Co($\eta^4$-$C_5Me_5H$). IR (hexane cast, $cm^{-1}$) 2951 (s), 2897 (m), 2856 (m), 2717 (m), 1447 (m), 1378 (m), 1357 (m), 1245 (s), 1162 (m), 1081 (m), 1038 (m), 900 (m), 833 (s), 796 (m), 751 (m), 688 (m), 629 (m); $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 4.33 (t, $J$ = 1.8 Hz, 2H, $Cp^{TMS}$), 4.11 (t, $J$ = 1.8 Hz, 2H, $Cp^{TMS}$), 2.58 (q, $J$ = 6.1 Hz, 1H, $C_5Me_5\underline{H}$), 2.02 (s, 6H, Me), 1.16 (s, 6H, Me), 0.43 (s, 9H, $SiMe_3$), 0.40 (d, $J$ = 6.1 Hz, 3H, Me); $^{13}C$ NMR (100 MHz, $C_6D_6$) $\delta$ 89.4, 85.0 ($Cp^{TMS}$), 84.4 ($Cp^{TMS}$), 56.6, 42.3, 20.4, 15.1, 12.8, 0.50 (TMS). $Cp^{TMS}$ ring quaternary carbon was not located. MS *m/z* calculated for $C_{18}H_{29}CoSi$ ($M^+$): 332.13705; found: 332.13481 (9%). MS *m/z* calculated for $C_{15}H_{20}Co$ ($M^+$ - $SiMe_3$): 259.08969; found: 259.08980 (100%).

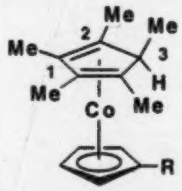
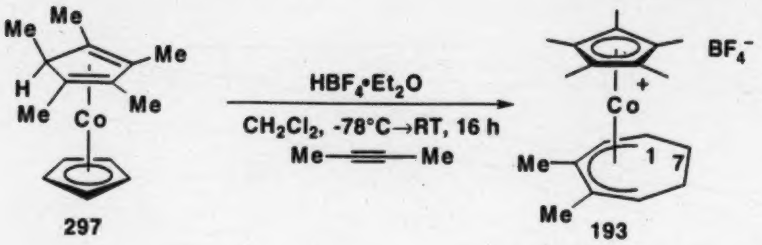


**Table 15**. $^{13}C$ NMR Data for $\eta^4$-Pentamethylcyclopentadiene Complexes

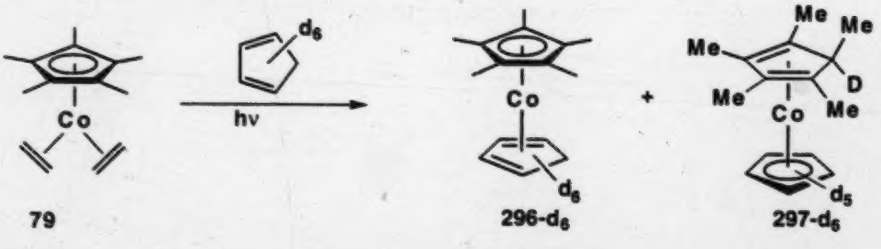
| | **297** | **298** | **299** | **300** |
|---|---|---|---|---|
| Cp | 80.8<br>--<br>-- | 81.7<br>80.3<br>92.3 | 80.4<br>76.9<br>a | 85.0<br>84.4<br>a |
| C1 | 56.7 | 56.4 | 56.7 | 56.6 |
| C2 | 89.0 | 88.6 | 88.5 | 89.4 |
| C3 | 41.4 | 45.0 | 43.0 | 42.3 |
| C4 | 20.4 | 20.2 | 20.4 | 20.4 |
| C5 | 12.6 | 12.1 | 12.8 | 12.8 |
| C6 | 15.2 | 14.6 | 14.9 | 15.1 |
| R group | -- | 10.3 | 32.1[b] | 0.50 |

[a] Quaternary carbon not located. [b] Resonance for the *t*-Bu methyl group only. *t*-Bu quaternary not located.



**$[(C_5Me_5)Co(3,4\text{-}Me_2\text{-}\eta^5\text{-}C_7H_7)]^+ BF_4^-$ (193).** In the drybox, the mixture of $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_5Me_5H)$ (**297**) and its isomer (29.4 mg, 0.113 mmol) was weighed out into a Schlenk flask. The flask was removed to the Schlenk line, where degassed dichloromethane (6 mL) was added. The solution was cooled to -78 °C and 2-butyne (44 µL, 5 equiv) was added. $HBF_4•Et_2O$ (18 µL, 1.1 equiv) was added and the solution was allowed to slowly warm to room temperature. All volatile material was removed *in vacuo* and the residue was purified by flash chromatography on silica gel, using 7% methanol-dichloromethane as the eluent. An orange band was collected and upon removal of solvent, an orange solid (32 mg, 70%) was obtained. The analytical sample was obtained by recrystallization from dichloromethane/diethyl ether. Crystals suitable for X-ray crystallographic analysis were obtained by layering diethyl ether on top of a solution in 5% acetonitrile/dichloromethane. For full data on this crystal structure, request report # JMS9605 from the Structure Determination Laboratory at the University of Alberta Department of Chemistry. IR ($CH_2Cl_2$ cast, $cm^{-1}$) 2990 (w), 2915 (w), 1489 (w), 1476 (w), 1437 (w), 1385 (m), 1089 (m), 1049 (s), 1032 (s), 518 (w); $^1H$ NMR (300 MHz, $CD_2Cl_2$) $\delta$ 4.67 (br d, $J_{2\text{-}1} = 9.1$ Hz, 1H, $H_2$), 4.40 (ddd, $J_{1\text{-}2} = 8.7$ Hz, $J_{1\text{-}7exo} \approx J_{1\text{-}7endo} = 4.4$ Hz, 1H, $H_1$), 4.04 (dd, $J_{5\text{-}6endo} = 4.0$ Hz, $J_{5\text{-}6exo} = 7.3$ Hz, 1H, $H_5$), 2.45 (dddd, $J_{7endo\text{-}7exo} = 16.7$ Hz, $J_{7endo\text{-}6endo} = 9.8$ Hz, $J_{7endo\text{-}6exo} = 8.8$ Hz, $J_{7endo\text{-}1} = 5.3$ Hz, 1H, $H_{7endo}$), 2.24 (s, 3H, $Me_3$), 2.00 (s, 3H, $Me_4$), 2.15-1.95 (m, 1H, $H_{6endo}$, obscured by Me), 1.77 (s, 15H, $C_5\underline{Me_5}$), 1.58 (dddd, $J_{7exo\text{-}7endo} = 15.9$ Hz, $J_{7exo\text{-}6exo} = 5.9$ Hz, $J_{7exo\text{-}1} = 3.3$ Hz, $J_{7exo\text{-}2} = 4$ Hz, 1H, $H_{7exo}$), 0.77 (dddd, $J_{6exo\text{-}6endo} = 16.5$ Hz, $J_{6exo\text{-}7endo} = 8.1$ Hz, $J_{6exo\text{-}7exo} = 5.9$ Hz, $J_{6exo\text{-}5} = 4.2$ Hz, 1H, $H_{6exo}$); $^1H$-

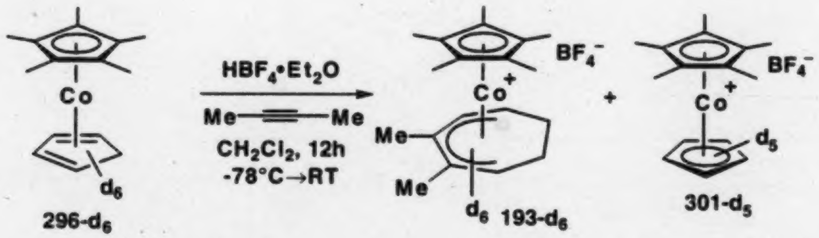
$^{1}H$ COSY (400 MHz, $CD_2Cl_2$) δ 4.67 ($H_2$) ↔ δ 2.24 (w, $Me_3$), δ 2.00 (w, $Me_4$); δ 4.40 ($H_1$) ↔ δ 2.45 ($H_{7endo}$), δ 1.58 ($H_{7exo}$); δ 4.04 ($H_5$) ↔ δ 2.07 ($H_{6endo}$), δ 0.77 ($H_{6exo}$); δ 2.45 ($H_{7exo}$) ↔ δ 1.58 ($H_{7exo}$), δ 0.77 (w, $H_{6exo}$); δ 2.07 ($H_{6endo}$) ↔ δ 1.58 ($H_{7exo}$), δ 0.77 ($H_{6exo}$); $^{13}C$ NMR (100 MHz, $CD_2Cl_2$) δ 110.9 (s, $C_3$), 107.4 (s, $C_4$), 98.0 (s, $\underline{C_5}Me_5$), 97.7 (d, $^{1}J_{CH}$ = 164.2 Hz, $C_2$), 93.5 (d, $^{1}J_{CH}$ = 149.7 Hz, $C_1$), 87.0 (d, $^{1}J_{CH}$ = 156.3 Hz, $C_5$), 35.9 (t, $^{1}J_{CH}$ = 130.2 Hz, $C_7$), 30.6 (t, $^{1}J_{CH}$ = 130.0 Hz, $C_6$), 19.8 (q, $^{1}J_{CH}$ = 128.3 Hz, $Me_3$), 18.6 (q, $^{1}J_{CH}$ = 126.2 Hz, $Me_4$), 9.3 (q, $^{1}J_{CH}$ = 128.8 Hz, $C_5\underline{Me_5}$); $^{1}H$-$^{13}C$ HETCORR (100 MHz, $CD_2Cl_2$) δ 97.7 ($C_2$) ↔ δ 4.67 ($H_2$); δ 93.5 ($C_1$) ↔ δ 4.40 ($H_1$); δ 87.0 ($C_5$) ↔ δ 4.04 ($H_5$); δ 35.9 ($C_7$) ↔ δ 2.45 ($H_{7endo}$), δ 1.58 ($H_{7exo}$); δ 30.6 ($C_6$) ↔ δ 2.07 ($H_{6endo}$), δ 0.77 ($H_{6exo}$); δ 19.8 ($Me_3$) ↔ δ 2.00 ($Me_4$); δ 18.6 ($Me_4$) ↔ δ 2.24 ($Me_4$); δ 9.3 ($C_5\underline{Me_5}$) ↔ δ 1.77 ($C_5\underline{Me_5}$); Long Range $^{1}H$-$^{13}C$ HETCORR (100 MHz, $CD_2Cl_2$) δ 2.24 ($Me_3$) ↔ δ 97.7 ($C_2$), δ 107.4 ($C_4$), δ 110.9 ($C_3$, strong); δ 2.00 ($Me_4$) ↔ δ 87.0 ($C_5$), δ 107.4 ($C_4$, strong), δ 110.9 ($C_3$); HMBC (300 MHz, $CD_2Cl_2$) δ 110.9 ($C_3$) ↔ δ 4.40 ($H_1$), δ 4.04 ($H_5$), δ 2.24 ($Me_3$), δ 2.00 ($Me_4$); δ 107.4 ($C_4$) ↔ δ 4.67 ($H_2$), δ 4.40 ($H_1$), δ 4.04 ($H_5$), δ 2.24 ($Me_3$), δ 2.00 ($Me_4$), δ 0.77 ($H_{6exo}$); δ 97.7 ($C_2$) ↔ δ 4.04 ($H_5$), δ 2.45 ($H_{7endo}$), δ 2.24 ($Me_3$); δ 93.5 ($C_1$) ↔ δ 4.67 ($H_2$), δ 2.45 ($H_{7endo}$), δ 1.58 ($H_{7exo}$), δ 0.77 ($H_{6exo}$); δ 87.0 ($C_5$) ↔ δ 2.45 ($H_{7endo}$), δ 2.00 ($Me_4$), δ 0.77 ($H_{6exo}$); δ 35.9 ($C_7$) ↔ δ 4.67 ($H_2$), δ 4.04 ($H_5$), δ 0.77 ($H_{6exo}$); δ 30.6 ($C_6$) ↔ δ 2.45 ($H_{7endo}$); δ 19.8 ($Me_3$) ↔ δ 4.67 ($H_2$), δ 2.45 ($H_{7endo}$); δ 18.6 ($Me_4$) ↔ δ 4.67 ($H_2$). Analysis calculated for $C_{19}H_{28}BCoF_4$: C, 56.74; H, 7.02; found: C, 56.842; H, 7.052.



(Eq. 107)

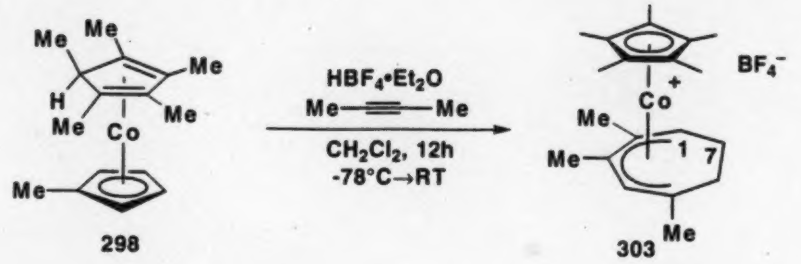
**($\eta^5$-$C_5Me_5$)Co($\eta^4$-$C_5D_6$) (296-$d_6$)** and **($\eta^5$-$C_5D_5$)Co($\eta^4$-$C_5Me_5D$) (297-$d_6$).** A 2:1 mixture of these two compounds was prepared by following the procedure for the

unlabelled analogue. IR (hexane cast, cm$^{1}$) 2946 (s), 2905 (s), 2854 (s), 2718 (w), 2286 (w), 2261 (w), 2189 (w), 2164 (w), 2117 (w), 2021 (s), 1971 (w), 1926 (w), 1559 (w), 1448 (m), 1380 (m), 1309 (m), 1244 (m), 1130 (w), 1069 (m), 1028 (m), 1007 (m), 956 (m), 852 (w), 765 (m), 745 (w), 727 (m), 702 (w), 647 (w), 603 (m), 529 (w), 513 (w), 477 (m), 440 (m); Data for (**296-d$_6$**): $^1$H NMR (400 MHz, $C_6D_6$) δ 1.74 (s, 15 H, $\eta^5$-$C_5Me_5$); $^2$H NMR (76.7 MHz, $C_6D_6$) δ 4.65 (s, 2D, $H_{2/3}$), 2.55 (s, 1D, $D_{5exo}$), 2.15 (s, 1D, $D_{5endo}$), 1.70 (2D, $D_{1/4}$). Data for (**297-d$_6$**): $^1$H NMR (400 MHz, $C_6D_6$) δ 1.97 (s, 6H), 1.1 (s, 6H), 0.35 (s, 3H); $^2$H NMR (76.7 MHz, $C_6D_6$) δ 4.30 (s, 5D, Cp), 2.40 (s, 1D, $\eta^4$-$C_5Me_5D$). MS *m/z* calculated for $C_{15}H_{15}D_6Co$ ($M^+$): 266.13519; found: 266.13472 (9%).



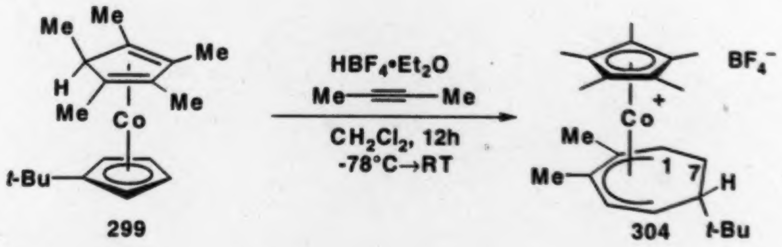
**296-d$_6$** **193-d$_6$** **301-d$_5$**

**($\eta^5$-$C_5Me_5$)Co($C_7HD_6Me_2$)$^+$ $BF_4^-$ (193-d$_6$).** Prepared according to the procedure for the unlabelled compound, except the purification step. All volatile material was removed *in vacuo* and the residue was recrystallized several times from dichloromethane/diethyl ether. The resulting light orange powder contained both Cp*(Cp-d$_5$)Co$^+$ OTf$^-$ (**301**-d$_6$) and the title compound. $^1$H NMR (300 MHz, $CDCl_3$) δ 5.22 (s, Cp*CpCo$^+$), 4.65 (br s, 1/7H, $H_2$), 4.39 (br s, 1/7H, $H_1$), 4.03 (br s, 1/7H, $H_5$), 2.45 (br s, 1/7H, $H_{7endo}$), 2.25 (s, 3H, Me), 2.05 (s, Cp*CoCp), 2.00 (s, 3H, Me), 1.77 (s, 15H, $C_5Me_5$). Other signals are not observed above baseline noise. $^2$H NMR (76.7 MHz, $CDCl_3$) δ 5.22 (s, Cp*CoCp), 4.65 (s, 1D, $D_2$), 2.39 (s, 1D, $D_1$), 4.03 (s, 1D, $D_5$), 2.45 (s, 1D, $D_{7endo}$), 2.0 (s, 1D, $D_{6endo}$), 1.55 (s, 1D, $D_{7exo}$), 0.75 (s, 1D, $D_{6exo}$).



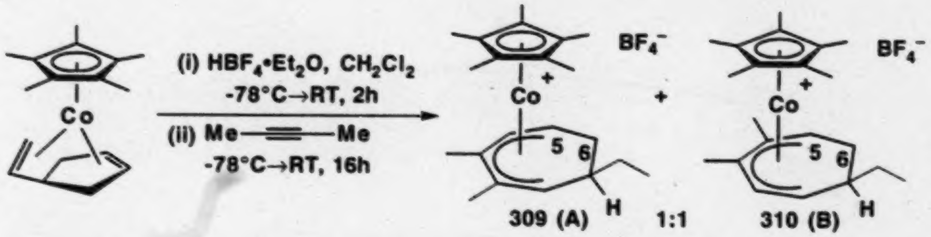
**[(C$_5$Me$_5$)Co(2,3,5-Me$_3$-η$^5$-C$_7$H$_6$)]$^+$ BF$_4^-$ (303).** A solution of (η$^5$-C$_5$H$_4$Me)Co(η$^4$-C$_5$Me$_5$H) (**298**) and its isomer (0.1327 g, 0.4837 mmol) in degassed dichloromethane (8 mL) was cooled to -78 °C in a dry-ice/acetone bath. 2-Butyne (0.2 mL, 10 equiv) was added by syringe. HBF$_4$•Et$_2$O (0.16 mL, 2.2 equiv) was then slowly added. The solution was then allowed to slowly warm to room temperature, with stirring. All volatile material was removed and the residue was purified by flash chromatography on a silica gel column, eluting with 7% methanol/dichloromethane. This yielded a dark red powder (0.111 g, 55%). IR (CH$_2$Cl$_2$ cast, cm$^{-1}$) 2993 (m), 2966 (m), 2912 (m), 2884 (m), 1454 (s), 1437 (s), 1384 (s), 1354(m), 1270 (m), 1092 (s), 1053 (vs), 1034 (s), 734 (s), 701 (m), 519 (m); $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 4.80 (br s, 1H, H$_4$), 3.91 (dd, $J_{5\text{-}6exo}$ = 7.3 Hz, $J_{5\text{-}6endo}$ = 4.0 Hz, 1H, H$_1$), 2.50 (dddd, $J_{7endo\text{-}7exo}$ = 16.7 Hz, $J_{7endo\text{-}6exo}$ = $J_{7endo\text{-}6endo}$ = 7.9 Hz, $J_{7endo\text{-}1}$ = 4.6 Hz, 1H, H$_{7endo}$), 2.24 (s, 3H, CH$_3$), 1.89 (s, 3H, CH$_3$), 1.68 (s, 15H, C$_5$$\underline{\text{Me}}_5$), 1.70-1.60 (m, 2H, H$_{6endo}$, H$_{7exo}$, overlaps with C$_5$Me$_5$), 1.52 (s, 3H, CH$_3$), 0.70 (ddd, $J_{6exo\text{-}6endo}$ = 14.5 Hz, $J_{6exo\text{-}7endo}$ = 8.1 Hz, $J_{6exo\text{-}7exo}$ = 5.5 Hz, 1H, H$_{6exo}$); $^1$H-$^1$H COSY (400 MHz, CD$_2$Cl$_2$) δ 3.91 (H$_1$) ↔ δ 2.50 (H$_{7endo}$), δ 1.67 (H$_{6endo,7exo}$); δ 2.50 (H$_{7endo}$) ↔ δ 1.67 (H$_{6endo,7exo}$), δ 0.70 (H$_{6exo}$); δ 1.67 (H$_{6endo,7exo}$) ↔ δ 0.70 (H$_{6exo}$); δ4.80 (H$_4$) ↔ δ 1.52 (w, Me), δ 1.89 (w, Me); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 115.7 (s, C$_3$), 105.6 (s, C$_2$), 97.4 (d, $^1J_{CH}$ = 158 Hz, C$_4$), 96.8 (s, $\underline{\text{C}}_5$Me$_5$), 82.7 (d, $^1J_{CH}$= 151 Hz, C$_1$), 38.4 (t, $^1J_{CH}$= 130 Hz, C$_7$), 35.4 (t, $^1J_{CH}$= 127 Hz, C$_6$), 27.6 (q, $^1J_{CH}$= 128 Hz, Me), 20.6 (q, $^1J_{CH}$= 129 Hz, Me), 18.9 (q, $^1J_{CH}$= 129 Hz, Me), 9.0 (q, $^1J_{CH}$= 129 Hz, C$_5$$\underline{\text{Me}}_5$); $^1$H-$^{13}$C HETCORR (100 MHz, CD$_2$Cl$_2$) δ

97.4 ($C_4$) ↔ δ 4.80 ($H_4$); δ 82.7 ($C_1$) ↔ δ 3.91 ($H_1$); δ 38.4 ($C_7$) ↔ δ 2.50 ($H_{7endo}$), δ 1.67 ($H_{7exo}$); δ 35.4 ($C_6$) ↔ δ 1.67 ($H_{6endo}$), δ 0.70 ($H_{6exo}$); δ 27.6 (Me) ↔ δ 1.52 (Me); δ 20.6 (Me) ↔ δ 1.89 (Me); δ 18.9 (Me) ↔ δ 2.24 (Me); δ 9.0 ($C_5\underline{Me}_5$) ↔ δ 1.68 ($C_5\underline{Me}_5$). Analysis calculated for $C_{20}H_{30}BCoF_4$: C, 57.72; H, 7.27; found: C, 57.471; H, 7.481.



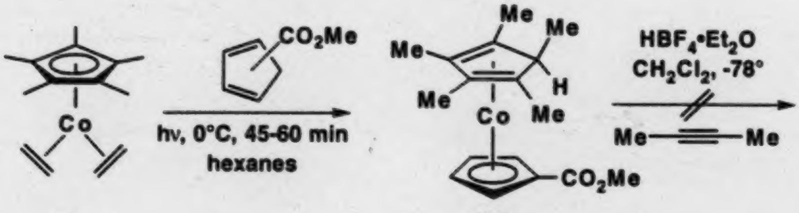
**[($C_5Me_5$)Co(6-*t*-Bu-2,3-$Me_2$-$\eta^5$-$C_7H_6$)]$^+$ $BF_4^-$ (304).** A solution of ($\eta^5$-$C_5H_4(C(CH_3)_3)$)Co($\eta^4$-$C_5Me_5H$) (**299**) and its isomer (0.1472 g, 0.4652 mmol) in degassed dichloromethane (8 mL) was prepared and cooled under nitrogen to -78 °C using a dry-ice/acetone bath. 2-butyne (0.36 mL, 10 equiv) was then added via syringe. $HBF_4$•$Et_2O$ (0.15 mL, 2 equiv) was added dropwise with stirring. The solution was then allowed to slowly warm overnight to room temperature. All volatile material was removed *in vacuo* and the residue was purified by flash chromatography on silica gel using 7% methanol/dichloromethane. A red powder (0.107 g, 50%) was obtained. IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3014 (m), 2989 (w), 2955 (s), 2914 (m), 2891 (m), 2868 (m), 2846 (m), 1481 (s), 1432 (m), 1394 (m), 1385 (s), 1365 (m), 1282 (w), 1244 (m), 1136 (w), 1071 (s), 1043 (s), 1033 (s), 976 (m), 839 (m), 733 (m), 520 (m); $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 5.00 (d, $J_{4\text{-}5}$ = 8.3 Hz, 1H, $H_4$), 4.15 (dd, $J_{5\text{-}4}$ = 8.3 Hz, $J_{5\text{-}6}$ = 5.0 Hz, 1H, $H_5$), 4.05 (dd, $J_{1\text{-}7endo}$ = $J_{1\text{-}7exo}$ = 3.5 Hz, 1H, $H_1$), 2.64 (ddd, $J_{7endo\text{-}7endo}$ = 16.0 Hz, $J_{7endo\text{-}6}$ = 11.8, $J_{7endo\text{-}1}$ = 4.0 Hz, 1H, $H_{7endo}$), 2.15 (ddd, $J_{7exo\text{-}7endo}$ = 16.3 Hz, $J_{7exo\text{-}6}$ = 5.3 Hz, $J_{7exo\text{-}1}$ = 3.2 Hz, 1H, $H_{7exo}$), 2.24 (s, 3H, $Me_3$), 1.88 (s, 3H, $Me_4$), 1.76 (s, 15H, $C_5\underline{Me}_5$), 0.84 (s, 9H, *t*-Bu), 0.21 (ddd, $J_{6\text{-}7endo}$ = 11.8, $J_{6\text{-}7exo}$ = $J_{6\text{-}5}$ = 5.2 Hz, 1H, $H_6$); $^1$H-$^1$H COSY (400 MHz, $CD_2Cl_2$)

δ 5.00 ($H_4$) ↔ δ 4.15 ($H_5$); δ 4.15 ($H_5$) ↔ δ 0.21 ($H_6$); δ 4.05 ($H_1$) ↔ δ 2.64 ($H_{7endo}$), δ 2.15 ($H_{7exo}$); δ 2.64 ($H_{7endo}$) ↔ δ 2.15 ($H_{7exo}$), δ 0.21 ($H_6$); δ 2.15 ($H_{7exo}$) ↔ δ 0.21 ($H_6$); $^{13}C$ NMR (100 MHz, $CD_2Cl_2$) δ 111.7 (s, $C_3$), 105.7 (s, $C_2$), 98.1 (s, $\underline{C}_5Me_5$), 98.1 (d, $^1J_{CH}$ = 168.3 Hz, $C_4$); 94.3 (d, $^1J_{CH}$ = 152.4 Hz, $C_5$); 84.6 (d, $^1J_{CH}$ = 150.5 Hz, $C_1$); 47.9 (d, $^1J_{CH}$ = 129.2 Hz, $C_6$); 44.8 (t, $^1J_{CH}$ = 127.7 Hz, $C_7$); 31.8 (s, $C_8$); 27.3 (q, $^1J_{CH}$ = 125.3 Hz, *t*-Bu); 21.2 (q, $^1J_{CH}$ = 129.0 Hz, Me); 18.6 (q, $^1J_{CH}$ = 129.4 Hz, Me); 9.4 (q, $^1J_{CH}$ = 128.7 Hz, $C_5\underline{Me}_5$); $^1H$-$^{13}C$ HETCORR (100 MHz, $CD_2Cl_2$) δ 98.1 ($C_4$) ↔ δ 5.00 ($H_4$); δ 94.3 ($C_5$) ↔ δ 4.15 ($H_5$); δ 84.6 ($C_1$) ↔ δ 4.05 ($H_1$); δ 47.9 ($C_6$) ↔ δ 0.21 ($H_6$); δ 44.8 ($C_7$) ↔ δ 2.64 ($H_{7endo}$), δ 2.15 ($H_{7exo}$); δ 27.3 (*t*-Bu) ↔ δ 0.84 (*t*-Bu); δ 21.2 (Me) ↔ δ 1.88 (Me); δ 18.6 (Me) ↔ δ 2.24 (Me); δ 9.4 ($C_5\underline{Me}_5$) ↔ δ 1.76 ($C_5\underline{Me}_5$); Analysis calculated for $C_{23}H_{36}BCoF_4$: C, 60.28; H, 7.92; found: C, 60.004; H, 7.766.



**[($C_5Me_5$)Co($\eta^5$-6-Et-3,4-$Me_2C_7H_6$)]$^+$ $BF_4^-$ (309). and [($C_5Me_5$)Co($\eta^5$-6-Et-2,3-$Me_2C_7H_6$)]$^+$ $BF_4^-$ (310).** In the drybox, ($C_5Me_5$)Co($\eta^4$-$C_7H_{10}$) (53.0 mg, 0.184 mmol) was placed into a flask and removed to the Schlenk line, where dichloromethane (6 mL) was added. The solution was cooled to -78 °C and $HBF_4$•$Et_2O$ (1.5 equiv, 41 µL) was added. The solution was slowly warmed to room temperature and stirred at that temperature for 2h. After recooling to -78 °C, 2-butyne (0.2 mL, excess) was added and the solution allowed to warm overnight to room temperature. The solvent was removed and the residue was purified by flash chromatography (silica gel), using 5% methanol/dichloromethane. After two recrystallizations from dichloromethane/diethyl ether, a light orange powder (28.6 mg, 36%) was obtained which was a 1:1 mixture of complexes **309** and **310**. IR ($CH_2Cl_2$ cast, $cm^{-1}$) 2960 (m), 2919 (m), 2860 (m), 1455 (m), 1384 (m), 1052 (s), 519 (m); $^1$H NMR (360 MHz, CDCl$_3$) For compound **309**: (A and B labels refer to **309** and **310**, respectively) δ 5.08 (d, *J* = 8.4 Hz, 1H, H$_{4a}$), 4.26 (ddd *J* = 8.0, 8.0, 4.4 Hz, 1H, H$_{5a}$), 3.98 (d, *J* = 3.6 Hz, 1H, H$_{1a}$), 2.90-2.72 (m, 2H, H$_{7a/7b}$), 2.27 (s, 3H, Me$_a$), 2.1-1.9 (m, 1H, H$_{6a}$, obscured by Me), 1.90 (s, 3H, Me$_a$), 1.78 (s, 15H, C$_5\underline{Me_5}$), 1.40-1.00 (series of m, $\underline{CH_2}$CH$_3$), 0.74 (t, *J* = 7.4 Hz, 3H, CH$_2\underline{CH_3}_a$), 0.19 (dddd, *J* = 13.8, 9.6, 4.5, 1.2 Hz, 1H, H$_{6a}$); $^1$H-$^1$H GCOSY (300 MHz, CDCl$_3$) δ 5.08 (H$_{4a}$) ↔ δ 4.26 (H$_{5a}$), δ 2.27 (w, Me$_a$), δ 1.90 (Me$_a$), δ 0.19 (H$_{6a}$); δ 4.26 (H$_{5a}$) ↔ δ 2.0 (H$_{6a}$); δ 3.98 (H$_{1a}$) ↔ δ 2.7 (H$_{7a}$); δ 2.8 (H$_{7a/7b}$) ↔ δ 2.05 (H$_{6a}$), δ 1.8 (H$_{6b}$), δ 1.2 (C$\underline{H}_2$CH$_3$), δ 1.0 (C$\underline{H}_2$CH$_3$), δ 0.19 (H$_{6a}$), δ -0.14 (H$_{6b}$); δ 2.0 (H$_{6a}$) ↔ 0.19 (H$_{6a}$). Several correlations from δ 1.4-1.0 to δ 0.80 and δ 0.74 arise from the ethyl groups.

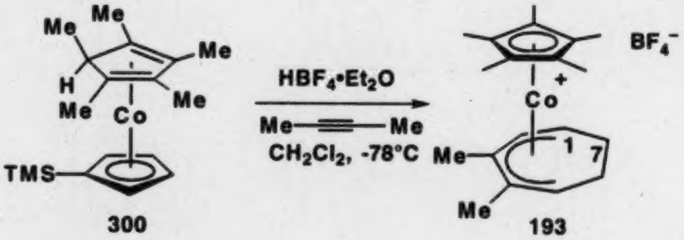
$^1$H NMR (360 MHz, CDCl$_3$) For compound **310**: (A and B labels refer to **309** and **310**, respectively) δ 4.59 (d, *J* = 9.6 Hz, 1H, H$_{2b}$), 4.29 (ddd, *J* = 10, 3.6, 1.5 Hz, 1H, H$_{1b}$), 3.82 (dd, *J* = 8.4, 4.5 Hz, 1H, H$_{5b}$), 2.90-2.72 (m, 2H, H$_{7a/7b}$), 2.26 (s, 3H, Me$_b$), 2.05 (s, 3H, Me$_b$), 1.85-1.75 (m, 1H, H$_{6b}$, obscured by Me), 1.79 (s, 15H, C$_5\underline{Me_5}$), 1.40-1.00 (series of m, $\underline{CH_2}$CH$_3$), 0.80 (t, *J* = 7.4 Hz, 3H, CH$_2\underline{CH_3}_b$), -0.14 (ddd, *J* = 12.6, 10.5, 4.5 Hz, 1H, H$_{6b}$); $^1$H-$^1$H GCOSY (300 MHz, CDCl$_3$) δ 4.59 (H$_{2b}$) ↔ δ 4.29 (H$_{1b}$), δ 2.26 (w, Me$_b$), δ 2.05 (Me$_b$); δ 4.29 (H$_{1b}$) ↔ δ 2.8 (H$_{7b}$); δ 3.82 (H$_{5b}$) ↔ δ 1.8 (H$_{6b}$), -0.14 (H$_{6b}$); δ 2.8 (H$_{7a/7b}$) ↔ δ 2.05 (H$_{6a}$), δ 1.8 (H$_{6b}$), δ 1.2 (C$\underline{H}_2$CH$_3$), δ 1.0 (C$\underline{H}_2$CH$_3$), δ 0.19 (H$_{6a}$), δ -0.14 (H$_{6b}$); δ 1.8 (H$_{6b}$) ↔ -0.14 (H$_{6b}$). Several correlations from δ 1.4-1.0 to δ 0.80 and δ 0.74 arise from the ethyl groups. Analysis calculated for C$_{21}$H$_{32}$BCoF$_4$: C, 58.63; H, 7.50; found: C, 58.883; H, 7.646.



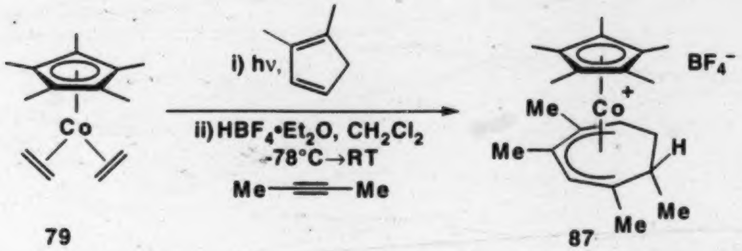
**79** **311**

**Reaction of Diene complex 311 with 2-butyne.** A solution of $(C_5Me_5)Co(C_2H_4)_2$ (**79**) (0.1129 g, 0.4511 mmol) and carbomethoxycyclopentadiene[246] (0.30 mL, 5 equiv) in hexane (30 mL) was photolyzed 90 min under a nitrogen purge. The solvent was removed and the residue was extracted with a small amount of pentane. The pentane extract was filtered through a Celite pad and the solvent was removed, leaving a deep red oily residue (0.1017 g, 71%). MS *m/z* calculated for $C_{17}H_{23}CoO_2$ ($M^+$): 318.10300; found: 318.10295 (16%). MS *m/z* calculated for $C_{16}H_{20}Co)_2$ ($M^+ - CH_3$): 303.07953; found: 303.07930 (100%).

A Schlenk flask was charged with $\eta^4$-Cp*Co($\eta^5$-$C_5H_4(CO_2Me)$ (**311**) (0.0647 g, 0.203 mmol) and dichloromethane (10 mL). The solution was cooled to -78°C and 2-butyne (0.16 mL, 10 equiv) was added, followed by $HBF_4{\bullet}Et_2O$ (30 μL, 1.0 equiv). The solution was allowed to warm to room temperature overnight. TLC analysis showed only cobalticenium products.



**Reaction of Diene Complex 300 with 2-butyne.** A solution of $(C_5Me_5)Co(TMS\text{-}C_5H_5)$ (**300**) (73.0 mg, 0.188 mmol) in degassed $CH_2Cl_2$ (10 mL) was cooled to -78°C under nitrogen. To this solution was added 2-butyne (0.2 mL, 10 equiv) and $HBF_4{\bullet}Et_2O$ (31 μL, 1.1 equiv). The solution was allowed to warm to room temperature over a 12 h period. The solvent was removed *in vacuo* and the product was isolated by flash chromatography on silica gel, using 5% methanol/ dichloromethane to elute the red-orange $\eta^5$-cycloheptadienyl **193**. The product was not completely pure by $^1$H NMR spectroscopy and the estimated yield was about 25%. The $^1$H NMR spectrum was identical to that obtained from the product prepared from Cp*CoCp, $HBF_4$ and butyne.



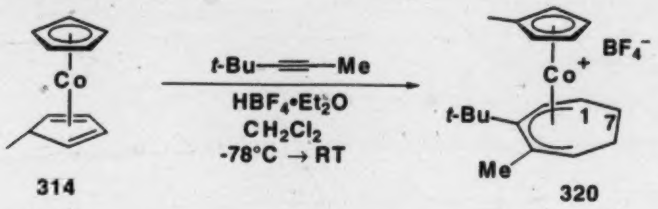
79

87

**$[(C_5Me_5)Co(2,3,5,6\text{-}Me_4\text{-}\eta^5\text{-}C_7H_5)]^+ BF_4^-$ (87) .** To a Schlenk flask was added $Cp^*Co(C_2H_4)_2$ (**79**) (0.1662 g, 0.6641 mmol) and hexane (40 mL). Dimethylcyclopentadiene (0.188 g, 2.0 mmol, 3 equiv) was added to the solution. The light orange solution was then photolyzed for 1h, under a slight nitrogen purge. The solvent was removed *in vacuo* and the residue was extracted with a small amount of pentane. The red pentane extract was filtered through a pad of Celite and the pentane was removed. A red oily residue (0.1673 g, 87%) remained and was used directly in the next step.

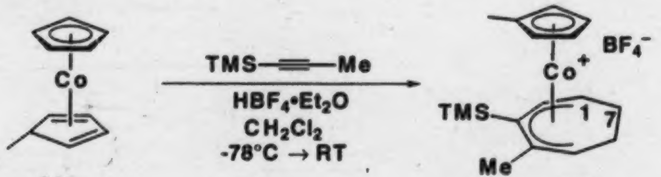
To a Schlenk flask was added $Cp^*Co(\eta^4\text{-}C_5H_4Me_2)$ (0.0674 g, 0.234 mmol) and dichloromethane (6 mL) under a nitrogen atmosphere. The solution was cooled to -78°C and 2-butyne (0.18 mL, 10 equiv) was added, followed by $HBF_4{\bullet}Et_2O$ (76 µL). The solution was allowed to warm slowly to room temperature over a 12 h period and the solvent was removed. The residue was purified by flash chromatography on silica gel, eluting with 5% methanol/dichloromethane. A red solid (0.034 g, 33%) was obtained. The $^1H$ NMR spectrum was identical with that of $Cp^*Co(C_7Me_4)$ (**87**) prepared from Cp*Co(allyl) (triflate) and 2-butyne.

## Chapter 5 Experimental Section



**$[(C_5H_4Me)Co(3\text{-}t\text{-}Bu\text{-}4\text{-}MeC_7H_7)]^+ BF_4^-$ (320).** In the drybox, $(C_5H_5)Co(\eta^4\text{-}1\text{-}Me\text{-}C_5H_5)$ **(314)** (0.1230 g, 0.6025 mmol) was weighed into a Schlenk flask and removed to the Schlenk line, where dichloromethane (10 mL) was added. The solution was cooled to -78 °C and 3,3-dimethyl-2-pentyne (0.56 mL, 7 equiv) was added, followed by $HBF_4{\bullet}Et_2O$ (0.20 mL, 2.2 equiv). Upon addition of the acid, the color of the solution deepened from orange to dark red. The mixture was allowed to warm to room temperature overnight with stirring. All volatile material was removed *in vacuo* and the residue redissolved in dichloromethane (3 mL). The product was precipitated by addition of diethyl ether (20 mL). Recrystallization from dichloromethane/diethyl ether gave a red solid (0.1983 g, 85%). IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3113 (m), 2968 (s), 1695 (w), 1481 (s), 1456 (s), 1416 (m), 1382 (s), 1344 (w), 1308 (w), 1283 (w), 1241 (w), 1173 (w), 1057 (s), 860 (m), 733 (w), 695 (w), 520 (m), 481 (w), 465 (w); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 5.48 (br s, 1H, Cp'), 5.38 (br s, 1H, Cp'), 5.30-5.24 (m, ddd by decoupling, $J_{1\text{-}2} = 9.6$ Hz, $J_{1\text{-}7endo} = 3.6$ Hz, $J_{1\text{-}7exo} = 2.0$ Hz, 1H, $H_1$), 5.20-5.14 (m, 2H, Cp' and $H_2$), 5.04 (br s, 1H, Cp'), 4.96 (dd, $J_{5\text{-}6endo} = 8.4$ Hz, $J_{5\text{-}6exo} = 5.4$ Hz, 1H, $H_5$), 2.87 (dddd, $J_{7endo\text{-}7exo} = 17.4$ Hz, $J_{7endo\text{-}6exo} = 11.7$ Hz, $J_{7endo\text{-}6endo} = 8.7$ Hz, $J_{7endo\text{-}1} = 3.6$ Hz, 1H, $H_{7endo}$), 2.37 (s, 3H, $Me_4$), 2.08 (s, 3H, Cp' Me), 2.02-1.90 (m, ddddd by decoupling, $J_{7exo\text{-}7endo} = 17$ Hz, $J_{7exo\text{-}6exo} = 5.9$ Hz, $J_{7exo\text{-}1} = 2.0$ Hz, $J_{7exo\text{-}6endo} \approx 0.8$ Hz, $J_{7exo\text{-}2} < 1$ Hz, 1H, $H_{7exo}$), 1.75-1.65 (m, ddddd by decoupling, $J_{6endo\text{-}6exo} = 12.5$ Hz, $J_{6endo\text{-}5} = J_{6endo\text{-}7endo} = 8.3$ Hz, $J_{6endo\text{-}2} = 1.8$ Hz, $J_{6endo\text{-}7exo} \approx 0.8$ Hz, 1H, $H_{6endo}$), 1.58 (s, 9H, t-Bu), 0.057 (dddd, $J_{6exo\text{-}6endo} = J_{6exo\text{-}7endo} = 11.6$ Hz, $J_{6exo\text{-}7exo} = J_{6exo\text{-}5} = 5.7$ Hz, 1H, $H_{6exo}$); $^1H$-

$^1$H GCOSY (300 MHz, $CDCl_3$) δ 5.48 (Cp') ↔ δ 5.38 (Cp'), δ 5.17 (Cp'), δ 5.04 (Cp'), 2.08 (w, Cp' Me); δ 5.38 (Cp') ↔ δ 5.17 (Cp'), δ 5.04 (Cp'), 2.08 (w, Cp' Me); δ 5.27 ($H_1$) ↔ δ 5.17 ($H_2$), δ 2.87 ($H_{7endo}$), 1.95 ($H_{7exo}$), δ 1.70 ($H_{6endo}$); δ 5.17 ($H_2$, Cp') ↔ δ 5.04 (Cp'), δ 2.87 ($H_{7endo}$), δ 2.37 (w, $Me_4$), 1.95 ($H_{7exo}$), δ 1.70 ($H_{6endo}$); δ 4.96 ($H_5$) ↔ δ 2.37 (w, $Me_4$), δ 1.70 ($H_{6endo}$), δ 0.057 ($H_{6exo}$); δ 2.87 ($H_{7endo}$) ↔ δ 1.95 ($H_{7exo}$), δ 1.70 ($H_{6endo}$), δ 0.057 ($H_{6exo}$); δ 1.95 ($H_{7exo}$) ↔ δ 0.057 ($H_{6exo}$); δ 1.70 ($H_{6endo}$) ↔ δ 0.057 ($H_{6exo}$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 134.3, 106.4, 104.2, 90.2, 87.9, 87.6, 87.00, 86.98, 86.8, 40.8 ($C_7$), 36.6, 32.3 (*t*-Bu), 25.35 ($Me_4$, $C_6$), 25.26 ($Me_4$, $C_6$), 13.0 ($C_5H_4\underline{Me}$); HMQC (300 MHz, $CDCl_3$, select data only) δ 90.2-86.8 ↔ δ 5.8-4.6; δ 40.8 ($C_7$) ↔ δ 2.87 ($H_{7endo}$), δ 1.90 ($H_{7exo}$); δ 32.3 (*t*-Bu) ↔ δ 1.58 (*t*-Bu); δ 25.35/25.26 ($Me_4$, $C_6$) ↔ δ 2.37 ($Me_4$), δ 1.70 ($H_{6endo}$), δ 0.057 ($H_{6exo}$); δ 13.0 ($C_5H_4\underline{Me}$) ↔ δ 2.08 ($C_5H_4\underline{Me}$). Electrospray MS *m/z* calculated for $C_{18}H_{26}Co$ ($M^+$-$BF_4$): 301.136649; found: 301.135900 (100%). Analysis calculated for $C_{18}H_{26}BCoF_4$: C, 55.70; H, 6.75; found: C, 55.383; H, 6.790.



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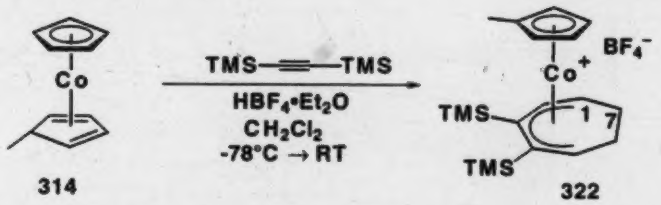
**[($C_5H_4Me$)Co(3-($SiMe_3$)-4-$MeC_7H_7$)]$^+$ $BF_4^-$ (321).** In the drybox, (Cp)Co($\eta^4$-1-Me-$C_5H_5$) **(314)** (0.0722 g, 0.354 mmol) was weighed into a Schlenk flask and removed to the Schlenk line, where dichloromethane (8 mL) was added. The solution was cooled to -78 °C and 1-(trimethylsilyl)-propyne (0.105 mL, 2 equiv) was added, followed by $HBF_4$•$Et_2O$ (0.115 mL, 2.2 equiv). Upon addition of the acid, the color of the solution deepened from orange to dark red. The mixture was allowed to warm to room temperature overnight, with stirring. All volatile material was removed *in vacuo*. The residue was purified by flash chromatography on silica gel, using 5%

methanol/dichloromethane as an eluent. A deep red band was collected and dried to give an orange solid (0.1131 g, 85%). IR ($CDCl_3$ cast, cm$^{-1}$) 3111 (w), 2958 (w), 2263 (w), 1694 (w), 1481 (m), 1455 (m), 1435 (m), 1414 (m), 1381 (w), 1344 (w), 1256 (s), 1056 (s), 916 (m), 842 (s), 763 (m), 727 (m), 647 (w), 624 (w), 520 (m), 409 (m); $^1$H NMR (360 MHz, $CDCl_3$) δ 5.64 (br s, 1H, Cp'), 5.4-5.3 (m, 2H, Cp' and $H_1$), 5.18 (br s, 1H, Cp'), 5.09 (d, $J_{2\text{-}1}$ = 9.6 Hz, 1H, $H_2$), 5.01 (dd, $J_{5\text{-}6endo}$ = 8.1 Hz, $J_{5\text{-}6exo}$ = 5.1 Hz, 1H, $H_5$), 4.97 (br s, Cp'), 2.94 (m, dddd by decoupling, $J_{7endo\text{-}7exo}$ = 17.5 Hz, $J_{7endo\text{-}6exo}$ = 11.2 Hz, $J_{7endo\text{-}6endo}$ = 8.5 Hz, $J_{7endo\text{-}1}$ = 3.9 Hz, 1H, $H_{7endo}$), 2.52 (s, 3H, $Me_4$), 2.06 (s, 3H, Cp' Me), 2.00 (m, dddd by decoupling, $J_{7exo\text{-}7endo}$ = 16.9 Hz, $J_{7exo\text{-}6exo}$ = 5.4 Hz, $J_{7exo\text{-}1}$ = small, $J_{7exo\text{-}6endo}$ = small, 1H, $H_{7exo}$), 1.85 (m, ddddd by decoupling, $J_{6endo\text{-}6exo}$ = 12.2 Hz, $J_{6endo\text{-}7endo}$ = $J_{6endo\text{-}5}$ = 8.3 Hz, $J_{6endo\text{-}1}$ < 1Hz, $J_{6endo\text{-}7exo}$ = 0.8 Hz, 1H, $H_{6endo}$), 0.36 (s, 9H, $SiMe_3$), 0.15 (m, dddd by decoupling, $J_{6exo\text{-}6endo}$ = 12.0 Hz, $J_{6exo\text{-}7endo}$ = 12.0 Hz, $J_{6exo\text{-}7exo}$ = 5.9 Hz, $J_{6exo\text{-}5}$ = 5.1 Hz, 1H, $H_{6exo}$); $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) δ 5.64 (Cp') ↔ δ 5.37 (Cp'), δ 5.18 (Cp'), δ 4.97 (Cp'), δ 2.06 (w, Cp' Me); δ 5.37 ($H_1$) ↔ δ 5.09 ($H_2$), δ 2.94 (w, $H_{7endo}$), δ 2.00 (w, $H_{7exo}$), δ 1.85 (w, $H_{6endo}$); δ 5.34 (Cp') ↔ δ 5.18 (Cp'), δ 4.97 (Cp'); δ 5.18 (Cp') ↔ δ 4.97 (Cp'); δ 5.09 ($H_2$) ↔ δ 2.00 (w, $H_{7exo}$); δ 5.01 ($H_5$) ↔ δ 1.85 ($H_{6endo}$), δ 0.15 ($H_{6exo}$); δ 2.94 ($H_{7endo}$) ↔ δ 2.00 ($H_{7exo}$), δ 1.85 ($H_{6endo}$), δ 0.15 ($H_{6exo}$); δ 2.00 ($H_{7exo}$) ↔ δ 0.15 ($H_{6exo}$); δ 1.85 ($H_{6endo}$) ↔ δ 0.15 ($H_{6exo}$). Note that no cross peak was observed for δ 2.00 ($H_{7exo}$) ↔ δ 1.85 ($H_{6endo}$). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 121.2 (s, $C_3$), 104.6 (s, Cp' quaternary), 101.5 (s, $C_4$), 95.8 (d, $^1J_{CH}$ = 167.8 Hz, $C_2$), 91.9 (d, $^1J_{CH}$ = 154.8 Hz, $C_1$), 88.6 (d, $^1J_{CH}$ = 159.6 Hz, $C_5$), 87.4$^a$ (d, $^1J_{CH}$ ≈ 180 Hz, Cp'), 86.4 (d, $^1J_{CH}$ = 182.7 Hz, Cp'), 85.4$^b$ (d, $^1J_{CH}$ ≈ 183 Hz, Cp'), 41.3 (t, $^1J_{CH}$ = 131.3 Hz, $C_7$), 27.0 (t, $^1J_{CH}$ = 132.9 Hz, $C_6$), 22.6 (q, $^1J_{CH}$ = 129.1 Hz, $Me_4$), 12.7 (q, $^1J_{CH}$ = 129.3 Hz, Cp' Me), -0.10 (q, $^1J_{CH}$ = 120.3 Hz, $SiMe_3$). $^a$Signal obscured in gated spectrum. $^b$Two carbon signals overlap. HMQC (300 MHz, $CDCl_3$) δ 95.8 ($C_2$) ↔ δ 5.09 ($H_2$); δ 91.9 ($C_1$) ↔ δ 5.35 ($H_1$); δ 88.6 ($C_5$) ↔ δ 5.01 ($H_5$); δ 87.4 (Cp') ↔ δ 5.18 (Cp'); δ 86.4 (Cp') ↔ δ 5.64

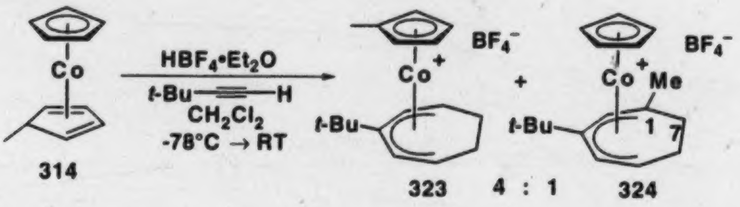
(Cp'); δ 85.4 (Cp') ↔ δ 5.35 (Cp'), δ 4.97 (Cp'); δ 41.3 ($C_7$) ↔ δ 2.94 ($H_{7endo}$), δ 2.00 ($H_{7exo}$); δ 27.0 ($C_6$) ↔ δ 1.85 ($H_{6endo}$), δ 0.15 ($H_{6exo}$); δ 22.6 ($Me_4$) ↔ δ 2.52 ($Me_4$); δ 12.7 (Cp' Me) ↔ δ 2.06 (Cp' Me); δ -0.10 ($SiMe_3$) ↔ δ 0.36 ($SiMe_3$); HMBC (300 MHz, $CDCl_3$) δ 121.2 ($C_3$) ↔ δ 5.01 ($H_5$), δ 2.52 ($Me_4$); δ 104.6 (Cp') ↔ δ 5.64 (Cp'), δ 5.35 (Cp'), δ 5.18 (Cp'), δ 4.97 (Cp'), δ 2.06 (Cp' Me); δ 101.5 ($C_4$) ↔ δ 5.09 ($H_2$), δ 5.01 ($H_5$), δ 2.52 ($Me_4$), δ 1.85 ($H_{6endo}$), δ 0.15 ($H_{6exo}$); δ 95.8 ($C_2$) ↔ δ 5.44 ($H_1$), δ 2.94 ($H_{7endo}$); δ 91.9 ($C_1$) ↔ δ 5.09 ($H_2$), δ 2.94 ($H_{7endo}$), δ 1.85 ($H_{6endo}$); δ 88.6 ($C_5$) ↔ δ 2.52 ($Me_4$), δ 1.85 ($H_{6endo}$), δ 0.15 ($H_{6exo}$); δ 87.4/86.4/85.4[a] (Cp') ↔ δ 5.64 (Cp'), δ 5.35 (Cp'), δ 5.18 (Cp'), δ 2.06 (Cp' Me); δ 41.3 ($C_7$) ↔ δ 5.09 ($H_2$), δ 0.15 ($H_{6exo}$); δ 27.0 ($C_6$) ↔ δ 5.01 ($H_5$), δ 2.94 ($H_{7endo}$); δ 22.6 (Cp' Me) ↔ δ 5.18 (Cp'). [a]Carbon signals unresolved. Electrospray MS *m/z* calculated for $C_{17}H_{26}CoSi$ ($M^+$-$BF_4$): 317.113577; found: 317.113890 (100%). Analysis calculated for $C_{17}H_{26}BCoF_4Si$: C, 50.51; H, 6.48; found: C, 50.331; H, 6.137.



**[($C_5H_4Me$)Co(3,4-($SiMe_3$)$_2$$C_7H_7$)]$^+$ $BF_4^-$ (322).** In the drybox, (Cp)Co($\eta^4$-1-Me-$C_5H_5$) **(314)** (0.1457 g, 0.7137 mmol) was weighed into a Schlenk flask and removed to the Schlenk line, where dichloromethane (15 mL) was added. The solution was cooled to -78 °C and bis(trimethylsilyl)acetylene (0.35 mL, 3 equiv) was added, followed by $HBF_4$•$Et_2O$ (0.231 mL, 2.2 equiv). Upon addition of the acid, the color of the solution deepened from orange to dark red. The mixture was allowed to warm to room temperature overnight, with stirring. All volatile material was removed *in vacuo* and the residue redissolved in dichloromethane (3 mL). The product was precipitated by addition of diethyl ether (20 mL). Recrystallization from dichloromethane/diethyl ether gave a

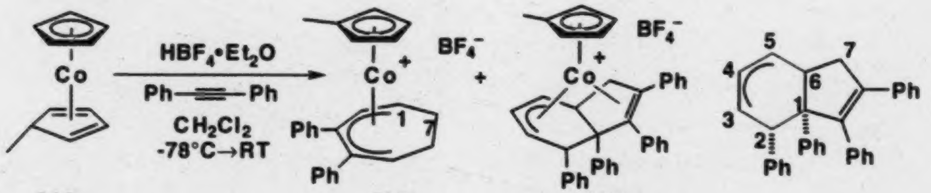
light orange solid (0.3104 g, 94%). IR ($CH_2Cl_2$ cast, cm$^1$) 3096 (w), 2957 (m), 1482 (m), 1455 (m), 1433 (m), 1254 (m), 1054 (s), 981 (m), 867 (s), 834 (s), 761 (m), 699 (w), 638 (w), 627 (w), 520 (m); $^1$H NMR (400 MHz, $CDCl_3$) δ 5.73 (br s, 1H, Cp'), 5.73-5.68 (m, dddd by decoupling, $J_{1\text{-}2}$ = 10.2 Hz, $J_{1\text{-}7endo}$ = 3.6 Hz, $J_{1\text{-}7exo}$ = 3.2 Hz, $J_{1\text{-}6endo}$ <1 Hz, 1H, $H_1$), 5.40 (br s, 1H, Cp'), 5.23 (dd, $J_{5\text{-}6endo}$ = 8.1 Hz, $J_{5\text{-}6exo}$ = 5.6 Hz, 1H, $H_5$), 5.21 (br s, 1H, Cp'), 5.08 (d, $J_{2\text{-}1}$ = 10.2 Hz, 1H, $H_2$), 4.90 (br s, 1H, Cp'), 3.09 (m, dddd by decoupling, $J_{7endo\text{-}7exo}$ = 18.0 Hz, $J_{7endo\text{-}6exo}$ = 11.8 Hz, $J_{7endo\text{-}6endo}$ = 8.3 Hz, $J_{7endo\text{-}1}$ = 3.6 Hz, 1H, $H_{7endo}$), 2.23 (s, 3H, Cp' Me), 2.20 (m, obscured by Me, $J_{obs}$ = 17 Hz, dddd by decoupling, $J_{7exo\text{-}7endo}$ = 17.1 Hz, $J_{7exo\text{-}6exo}$ = 5.9 Hz, $J_{7exo\text{-}6endo}$ = 2.1 Hz, $J_{7exo\text{-}1}$ = 3.2 Hz, 1H, $H_{7exo}$), 1.75-1.65 (m, dddd by decoupling, $J_{6endo\text{-}6exo}$ = 11.9 Hz, $J_{6endo\text{-}7endo}$ = 8.3 Hz, $J_{6endo\text{-}5}$ = 8.1 Hz, $J_{6endo\text{-}7exo}$ = 2.1 Hz, 1H, $H_{6endo}$), 0.55 (s, 9H, $SiMe_3$), 0.41 (s, 9H, $SiMe_3$), 0.042 (dddd, $J_{6exo\text{-}6endo}$ = $J_{6exo\text{-}7endo}$ = 12.6 Hz, $J_{6exo\text{-}7exo}$ = $J_{6exo\text{-}5}$ = 6.3 Hz, 1H, $H_{6exo}$); $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) δ 5.73 (Cp') ↔ δ 5.40 (Cp'), δ 5.21 (Cp'), δ 4.90 (Cp'); δ 5.70 ($H_1$) ↔ δ 5.08 ($H_2$), δ 3.09 ($H_{7endo}$), δ 2.20 (w, $H_{7exo}$), δ 1.70 ($H_{6endo}$); δ 5.40 (Cp') ↔ δ 5.21 (Cp'), δ 4.90 (Cp'); δ 5.23 ($H_5$) ↔ δ 1.70 ($H_{6endo}$), δ 0.04 ($H_{6exo}$); δ 5.21 (Cp') ↔ δ 4.90 (Cp'); δ 5.08 ($H_2$) ↔ δ 2.20 (w, $H_{7exo}$); δ 3.09 ($H_{7endo}$) ↔ δ 2.20 ($H_{7exo}$), δ 1.70 ($H_{6endo}$), δ 0.04 ($H_{6exo}$); δ 2.20 ($H_{7exo}$) ↔ δ 0.04 ($H_{6exo}$); δ 1.70 ($H_{6endo}$) ↔ δ 0.04 ($H_{6exo}$); $^{13}$C NMR (100 MHz, $CDCl_3$, $^1J_{CH}$ values obtained from HMQC spectrum) δ 119.9 (s, $C_3$), 106.8 (s, $C_4$), 105.0 (s, Cp' ring quaternary), 99.4 (d, $^1J_{CH}$ = 168 Hz, $C_2$), 95.3 (d, $^1J_{CH}$ = 156 Hz, $C_1$), 91.7 (d, $^1J_{CH}$ = 158 Hz, Cp'), 88.1 (d, $^1J_{CH}$ = 184 Hz, Cp'), 86.6 (d, $^1J_{CH}$ = 182 Hz, Cp'), 85.0$^a$ (d, $^1J_{CH}$ = 186 Hz, $C_5$), 84.6 (d, $^1J_{CH}$ = 184 Hz, Cp'), 42.2 (t, $^1J_{CH}$ = 128 Hz, $C_7$), 26.5 (t, $^1J_{CH}$ = 133 Hz, $C_6$), 13.5 (q, $^1J_{CH}$ = 128 Hz, Cp' Me), 2.2 (q, $^1J_{CH}$ = 117 Hz, $SiMe_3$), 1.6 (q, $^1J_{CH}$ = 120 Hz, $SiMe_3$). $^a$*J* value appears abnormally large. HMQC (300 MHz, $CDCl_3$) δ 99.4 ($C_2$) ↔ δ 5.08 ($H_2$); δ 95.3 ($C_1$) ↔ δ 5.70 ($H_1$); δ 91.7 (Cp') ↔ δ 5.21 (Cp'); δ 88.1 (Cp') ↔ δ 5.40 (Cp'); δ 86.6 (Cp') ↔ δ 5.73 (Cp'); δ 85.0 ($C_5$) ↔ δ 5.23 ($H_5$); δ 84.6 (Cp') ↔ δ 4.90 (Cp'); δ 42.2 ($C_7$) ↔ δ 3.09 ($H_{7endo}$), δ 2.20 ($H_{7exo}$); δ 26.5 ($C_6$) ↔ δ

1.70 ($H_{6endo}$), δ 0.04 ($H_{6exo}$); δ 13.5 (Cp' Me) ↔ δ 2.23 (Cp' Me); δ 2.2 ($SiMe_3$) ↔ δ 0.55 ($SiMe_3$); δ 1.6 ($SiMe_3$) ↔ δ 0.41 ($SiMe_3$). Analysis calculated for $C_{19}H_{32}BCoF_4Si_2$: C, 49.36; H, 6.98; found: C, 49.192; H, 7.115.



**$[(C_5H_4Me)Co(3\text{-}t\text{-}BuC_7H_8)]^+ BF_4^-$ (323)** and **$[(C_5H_5)Co(1\text{-}Me\text{-}3\text{-}t\text{-}BuC_7H_7)]^+ BF_4^-$ (324).** In the drybox, $(C_5H_5)Co(\eta^4\text{-}1\text{-}Me\text{-}C_5H_5)$ (**314**) (0.1463 g, 0.7166 mmol) was weighed into a Schlenk flask and removed to the Schlenk line, where dichloromethane (12 mL) was added. The solution was cooled to -78 °C and 3,3-dimethyl-1-butyne (0.62 mL, 7 equiv) was added, followed by $HBF_4{\bullet}Et_2O$ (0.23 mL, 2.2 equiv). Upon addition of the acid, the color of the solution deepened from orange to dark red. The mixture was allowed to warm to room temperature overnight with stirring. All volatile material was removed *in vacuo* and the residue redissolved in dichloromethane (3 mL) and filtered through a Celite pad. The product was precipitated by addition of diethyl ether (20 mL). Recrystallization from dichloromethane/diethyl ether gave an orange powder (0.2364 g, 88%). The product consisted of a 4:1 mixture of $(C_5H_4Me)Co(3\text{-}t\text{-}Bu\text{-}C_7H_8)$ (**323**) and $(C_5H_5)Co(3\text{-}t\text{-}Bu\text{-}5\text{-}Me\text{-}C_7H_7)$ (**324**). Major isomer **323**: IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3114 (m), 2968 (m), 2876 (m), 1497 (w), 1480 (m), 1411 (m), 1374 (m), 1266 (w), 1053 (s), 871 (m), 735 (m), 699 (w), 521 (m), 466 (w); $^1H$ NMR (300 MHz, $CDCl_3$) δ 5.51 (t, $J$ = 1.9 Hz, 2H, Cp'H), 5.46 (d, $J$ = 9.0 Hz, 2H, $H_{2/4}$), 5.38 (t, $J$ = 2.0 Hz, 2H, Cp'), 5.30-5.20 (m, 2H, $H_{1/5}$), 2.50-2.40 (m, 2H, $H_{6endo/7endo}$), 2.00 (s, 3H, Me), 1.56 (s, 9H, $t$-Bu), 1.25-1.15 (m, 2H, $H_{6exo/7exo}$); $^1H$-$^1H$ GCOSY (300 MHz, $CDCl_3$) δ 5.51 (Cp') ↔ δ 5.38 (Cp'); δ 5.46 ($H_{2/4}$) ↔ δ 5.25 ($H_{1/5}$); δ 5.25 ($H_{1/5}$) ↔ δ 2.45 ($H_{6/7endo}$), δ 1.20 ($H_{6/7exo}$); δ 2.45 ($H_{6/7endo}$) ↔ δ 1.20 ($H_{6/7exo}$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 132.7 ($C_3$), 129.2

(Cp' quaternary), 89.6 ($C_{2/4}$), 87.5 (Cp'), 87.0 (Cp'), 85.4 ($C_{1/5}$), 36.5 (*t*-Bu quaternary), 33.7 ($C_{6/7}$), 31.2 (*t*-Bu), 13.2 (Cp' Me). Data for minor isomer **324**: $^1$H NMR (300 MHz, $CDCl_3$, partial data only) δ 5.58 (s, 1H, $H_2$), 5.43 (s, 5H, Cp), 5.40-5.35 (m, obscured, 2H, $H_{4/5}$), 2.80 (dddd, *J* = 15.9, 8.4, 8.4, 4.5 Hz, 1H, $H_{7endo}$), 2.06-1.92 (m, obscured by Me), 1.84-1.76 (m, obscured by *t*-Bu), 1.84 (s, 3H, Me), 1.58 (s, 9H, *t*-Bu), 0.83 (ddd, *J* = 14.1, 8.4, 6.0 Hz, 1H, $H_{6exo}$); $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) δ 5.58 ($H_2$) ↔ δ 5.37 (w, $H_{4/5}$), δ 1.84 (w, Me); δ 5.37 ($H_{4/5}$) ↔ δ 2.80 ($H_{7endo}$); δ 2.80 ($H_{7endo}$) ↔ δ 2.00 ($H_{7exo}$), δ 1.80 ($H_{6endo}$), δ 0.83 ($H_{6exo}$); δ 2.00 ($H_{7exo}$) ↔ δ 1.80 ($H_{6endo}$), δ 0.83 ($H_{6exo}$); δ 1.80 ($H_{6endo}$) ↔ δ 0.83 ($H_{6exo}$). Analysis calculated for $C_{17}H_{24}BCoF_4$: C, 54.58; H, 6.47; found: C, 54.614; H, 6.326.



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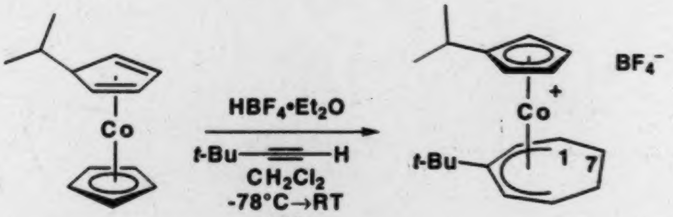
**[$(C_5H_4Me)Co(3,4\text{-}Ph_2C_7H_7)]^+$ $BF_4^-$ (325) and [$(C_5H_4Me)$Co(3-5η–8-9η-1,2,8,9-tetraphenylbicyclo[4.3.0]nona-4,8-dien-3-yl )]$^+$ $BF_4^-$ (326).** In the drybox, a Schlenk flask was charged with CpCo(η$^4$-$C_5H_5Me$) (**314**) (0.2299 g, 1.126 mmol). The flask was removed to the Schlenk line, where dichloromethane (25 mL) was added, followed by diphenylacetylene (2.00 g, 10 equiv). The flask was cooled to -78°C and $HBF_4$•$Et_2O$ (0.365 mL, 2.2 equiv) was added by syringe. The flask was allowed to warm slowly to room temperature. The solvent was removed and the residue was triturated with pentane to remove excess diphenylacetylene. The remaining residue was purified by column chromatography on silica gel, eluting with 5% methanol/dichloromethane. A dark red fraction was obtained and dried to give a red powder (0.2977g, 41%) of the bis adduct **326**. A second light orange fraction was collected and dried to give an orange powder (60.6 mg, 10%) of the diphenylcycloheptadienyl cobalt complex (**325**). The remainder of the material balance is unknown. In a similar experiment with 3 equivalents of alkyne, 32% of the bis adduct **326** and 23% of the monoadduct **325** were isolated.

Data for the bis adduct **326**: IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3058 (m), 2926 (w), 1599 (m), 1575 (w), 1494 (s), 1478 (m), 1455 (m), 1443 (m), 1425 (m), 1386 (w), 1312 (m), 1267 (m), 1221 (w), 1160 (m), 1058 (s), 926 (w), 898 (w), 868 (m), 847 (m), 773 (s), 734 (s), 700 (s), 631 (w), 612 (m), 595 (w), 562 (m), 544 (m), 521 (m), 487 (w), 462 (w); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.62-7.46 (br m, 2H, $H_{Ph}$), 7.49 (t, $J$ = 7.2 Hz, 2H, $H_{Ph}$), 7.40-7.40 (m, 4H, $H_{Ph}$), 7.00-6.80 (m, 11H, $H_{Ph}$ and $H_3$), 6.75 (t, $J$ = 7.5 Hz, 2H, $H_{Ph}$), 6.35 (d, $J_{5\text{-}6}$ = 5.5 Hz, 1H, $H_5$), 6.22 (d, $J$ = 7.9 Hz, 2H, $H_{Ph}$), 5.24 (br s, 1H, Cp'), 5.11 (t, $J_{4\text{-}6} = J_{4\text{-}5}$ = 6.8 Hz, 1H, $H_4$), 4.91[a] (br s, 2H, Cp'), 4.50 (br s, 1H, Cp'), 4.35 (d, $J_{2\text{-}3}$ = 5.1 Hz, 1H, $H_2$), 4.19 (d, $J_{7a\text{-}7b}$ = 15.2 Hz, 1H, $H_{7a}$), 3.31[b] (dd, $J_{7b\text{-}7a}$ = 14.7 Hz, $J_{7b\text{-}6}$ = 3.0 Hz, 1H, $H_{7b}$), 2.77 (br s, 1H, $H_6$), 1.64 (s, 3H, Cp' Me). [a] Depending on concentration, this signal is resolved into two separate Cp' singlets at δ 4.92 and δ 4.86. [b] Small $J$ value is not always well resolved. $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) δ 6.89 ($H_3$) ↔ δ 6.35 (w, $H_5$), δ 5.11 ($H_4$), δ 4.35 ($H_2$); δ 6.78 ($H_{Ph}$) ↔ δ 6.22 ($H_{Ph}$); δ 6.35 ($H_5$) ↔ δ 5.11 ($H_4$), δ 2.77 ($H_6$); δ 5.24 (Cp') ↔ δ 4.91 (Cp'), δ 4.50 (Cp'), δ 1.64 (w, Cp' Me); δ 5.11 ($H_4$) ↔ δ 2.77 (w, $H_6$); δ 4.91 (Cp') ↔ δ 4.50 (Cp'), δ 1.64 (w, Cp' Me); δ 4.50 (Cp') ↔ δ 1.64 (w, Cp' Me); δ 4.19 ($H_{7a}$) ↔ δ 3.31 ($H_{7b}$), δ 2.77 (w, $H_6$); δ 3.31 ($H_{7b}$) ↔ δ 2.77 ($H_6$); $^{13}$C (100 MHz, $CDCl_3$) δ 138.4 (s, $C_{Ph}$), 136.5 (s, $C_{Ph}$), 136.0 (s, $C_{Ph}$), 135.1[a] ($C_{Ph}$), 134.9[a] (s, $C_{Ph}$), 130.8[a] ($C_{Ph}$), 130.4[a] ($C_{Ph}$), 129.7[a] ($C_{Ph}$), 129.2[a] ($C_{Ph}$), 128.9[a] ($C_{Ph}$), 128.5[a] (2$C_{Ph}$), 128.4[a] (2$C_{Ph}$), 127.4[a] (2$C_{Ph}$), 127.2[a] (2$C_{Ph}$), 110.2 (s, $C_9$), 104.2 (s, Cp' quaternary), 95.6 (d, $^1J_{CH}$ = 182.7 Hz, Cp'), 94.2 (d, $^1J_{CH}$ = 176.9 Hz, Cp'), 93.2 (d, $^1J_{CH}$ = 185.6 Hz, Cp'), 91.7 (d, $^1J_{CH}$ = 171.1 Hz, $C_4$), 91.5 (d, $^1J_{CH}$ = 169.7 Hz, $C_5$), 88.5 (d, $^1J_{CH}$ = 185.6 Hz, Cp'), 81.8 (d, $^1J_{CH}$ = 168.2 Hz, $C_3$), 64.0 (s, $C_1$), 52.4 (d, $^1J_{CH}$ = 131.1 Hz, $C_2$), 48.0 (t, $^1J_{CH}$ = 126.6 Hz, $C_7$), 38.6 (d, $^1J_{CH}$ = 138.8 Hz, $C_6$), 12.6 (q, $^1J_{CH}$ = 128.1 Hz, Cp' Me). [a] Phenyl carbon signals do not resolve in the gated decoupled $^{13}$C spectrum. HMQC[a] (300 MHz, $CDCl_3$) δ 95.6 (Cp') ↔ δ 4.50

(Cp'); δ 94.2 (Cp') ↔ δ 4.91 (Cp'); δ 93.2 (Cp') ↔ δ 4.91 (Cp'); δ 91.7 ($C_4$) ↔ δ 5.11 ($H_4$); δ 91.5 ($C_5$) ↔ δ 6.35 ($H_5$); δ 88.5 (Cp') ↔ δ 5.24 (Cp'); δ 81.8 ($C_3$) ↔ δ 6.89 ($H_3$); δ 52.4 ($C_2$) ↔ δ 4.35 ($H_2$); δ 48.0 ($C_7$) ↔ δ 4.19 ($H_{7a}$), δ 3.31 ($H_{7b}$); δ 38.6 ($C_6$) ↔ δ 2.77 ($H_6$); δ 12.6 (Cp' Me) ↔ δ 1.64 (Cp' Me). [a] Phenyl carbon signals do not resolve in either the HMQC or HMBC spectrum. HMBC[a] (300 MHz, $CDCl_3$) δ 138.4 ($C_{Ph}$) ↔ δ 4.35 ($H_2$); δ 136.0 ($C_{Ph}$) ↔ δ 6.78 ($H_{Ph}$); δ 135.1 ($C_{Ph}$) ↔ δ 7.5 ($H_{Ph}$); δ 130.4 ($C_{Ph}$) ↔ δ 4.19 ($H_{7a}$); δ 128.4 ($C_{Ph}$) ↔ δ 4.35 ($H_2$); δ 127.4 ($C_{Ph}$) ↔ δ 6.22 ($H_{Ph}$); δ 110.2 ($C_9$) ↔ δ 4.35 ($H_2$), δ 4.19 ($H_{7a}$); δ 104.2 (Cp' quaternary) ↔ δ 5.24 (Cp'), δ 4.91 (Cp'), δ 4.50 (Cp'), δ 1.64 (Cp' Me); δ 95.6 (Cp') ↔ δ 5.24 (Cp'), δ 4.91 (Cp'), δ 1.64 (Cp' Me); δ 94.2/93.2[b] (Cp') ↔ δ 5.24 (Cp'), δ 4.91 (Cp'), δ 4.50 (w, Cp'), δ 1.64 (Cp' Me); δ 91.7/91.5[b] ($C_4$/$C_5$) ↔ δ 6.89 ($H_3$), δ 4.35 ($H_2$), δ 4.19 ($H_{7a}$); δ 88.5 (Cp') ↔ δ 4.91 (Cp'), δ 4.50 (w, Cp'), δ 1.64 (Cp' Me); δ 81.8 ($C_3$) ↔ δ 6.35 ($H_5$), δ 4.35 ($H_2$); δ 64.0 ($C_1$) ↔ δ 6.89 ($H_3$), δ 6.35 ($H_5$), δ 6.22 ($H_{Ph}$); δ 4.35 ($H_2$), δ 4.19 ($H_{7a}$); δ 52.4 ($C_3$) ↔ δ 5.11 ($H_4$); δ 38.6 ($C_6$) ↔ δ 5.11 ($H_4$), δ 4.35 ($H_2$). [a] Phenyl carbon signals do not resolve in either the HMQC or HMBC spectrum. [b]Signals not well resolved. Analysis calculated for $C_{39}H_{35}BCoF_4$: C, 72.13; H, 5.43; found: C, 69.967; H, 5.263. Electrospray MS *m/z* calculated for $C_{39}H_{34}Co$ ($M^+ - HBF_4$): 561.199249; found: 561.198751 (100%).

Data for the mono adduct **325**: IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3106 (w), 3050 (vw), 3045 (vw), 2950 (vw), 2925 (vw), 2861 (w), 1445 (w), 1433 (w), 1411 (w), 1383 (w), 1366 (w), 1284 (w), 1181 (w), 1157 (w), 1047 (s), 897 (w), 866 (w), 848 (w), 840 (w), 789 (w), 766 (m), 701 (m), 626 (w), 598 (w), 558 (w), 534 (w), 521 (w); $^1H$ NMR (400 MHz, $CD_2Cl_2$) δ 7.60-7.20 (series of m, 10H, $H_{Ph}$), 5.66 (br s, 1H, Cp'), 5.63 (dd, $J_{5\text{-}6endo}$ = 8.1 Hz, $J_{5\text{-}6exo}$ = 4.8 Hz, 1H, $H_5$), 5.35 (m, 2H, $H_1$, $H_2$), 5.24 (br s, 1H, Cp'), 5.22 (br s, 1H, Cp'), 5.12 (br s, 1H, Cp'), 3.08 (dddd, $J_{7endo\text{-}7exo}$ = 17.5 Hz, $J_{7endo\text{-}6exo}$ = $J_{7endo\text{-}6endo}$ = 9.0 Hz, $J_{7endo\text{-}1}$ = 0.8 Hz, 1H, $H_{7endo}$), 2.29 (dddd, $J_{6endo\text{-}6exo}$ = 13.6 Hz, $J_{6endo\text{-}7endo}$ = 8.7 Hz, $J_{6endo\text{-}5}$ = 8.4 Hz, $J_{6endo\text{-}7exo}$ = 2.5 Hz, 1H, $H_{6endo}$), 2.02 (br dd, dddd by decoupling, $J_{7exo\text{-}7endo}$ = 17.3 Hz, $J_{7exo\text{-}6exo}$ = 5.1 Hz, $J_{7exo\text{-}6endo}$ = 2.5 Hz,

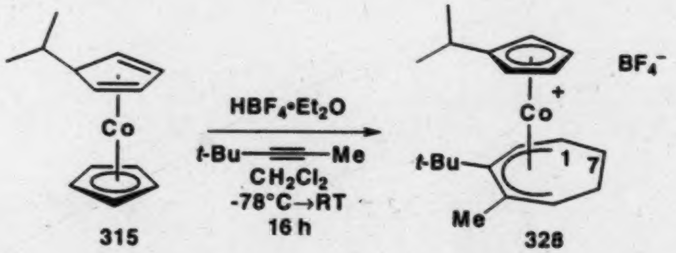
$J_{7exo\text{-}1}$ <2 Hz, 1H, $H_{7exo}$), 1.77 (s, 3H, Cp' Me), 0.79 (m, ddddd by decoupling, $J_{6exo\text{-}6endo}$ = 14.5 Hz, $J_{6exo\text{-}7endo}$ = 10.0 Hz, $J_{6exo\text{-}7exo}$ = 5.1 Hz, $J_{6exo\text{-}5}$ = 4.8 Hz, $J_{obs}$ = 1.9 Hz, 1H, $H_{6exo}$); $^1H$-$^1H$ GCOSY (300 MHz, $CD_2Cl_2$) δ 5.66 (Cp') ↔ δ 5.23$^a$ (Cp'), δ 5.12 (Cp'); δ 5.63 ($H_5$) ↔ δ 2.29 ($H_{6endo}$), δ 0.79 ($H_{6exo}$); δ 5.35 ($H_{1/2}$) ↔ δ 3.08 ($H_{7endo}$), δ 2.02 ($H_{7exo}$); δ 5.23$^a$ (Cp') ↔ δ 5.12 (Cp'); δ 3.08 ($H_{7endo}$) ↔ δ 2.29 ($H_{6endo}$), δ 2.02 ($H_{7exo}$), δ 0.79 ($H_{6exo}$); δ 2.29 ($H_{6endo}$) ↔ δ 2.02 ($H_{7exo}$), δ 0.79 ($H_{6exo}$); δ 2.02 ($H_{7exo}$) ↔ δ 0.79 ($H_{6exo}$);



315 327

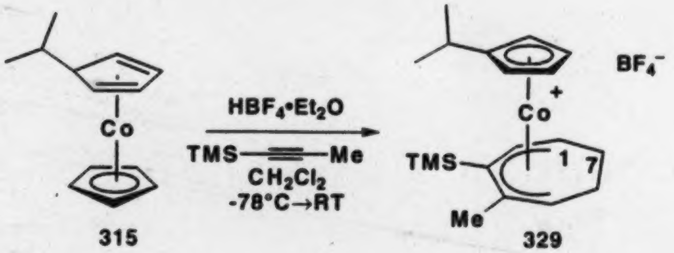
**$[(C_5H_4{}^iPr)Co(\eta^5\text{-}3\text{-}t\text{-}BuC_7H_8)]^+\ BF_4^-$ (327).** In the drybox, a flask was charged with $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}1\text{-}{}^iPrC_5H_5)$ **(315)** (0.1047 g, 0.4509 mmol) and removed to the Schlenk line, where dichloromethane (10 mL) was added. The solution was cooled to -78 °C and $HBF_4{\bullet}Et_2O$ (0.146 mL, 2.2 equiv) was added, turning the solution a deep red color. Upon addition of 3,3-dimethyl-1-butyne (0.167 mL, 3 equiv), the color turned to green. After 2 h at -78 °C, the solution had turned a deep red color. Allowing the solution to warm to room temperature did not result in any further color change. Removal of all volatile material gave a dark oily residue. The compound was purified by flash chromatography (silica gel) using 5% methanol-dichloromethane. After a red band was collected and the solvent was removed, there remained a red residue (0.0456 g, 25%). IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3112 (m), 2967 (s), 2874 (m), 1479 (s), 1399 (m), 1373 (m), 1312 (w), 1283 (w), 1259 (w), 1054 (s), 916 (m), 862 (m), 698 (w), 520 (m); $^1H$ NMR (360 MHz, $CDCl_3$) δ 5.60-5.50 (m, 4H, 2Cp$^i$ and $H_{2/4}$), 5.30-5.20 (m, 4H, 2Cp$^i$ and $H_{1/5}$), 2.75 (septet, $J$ = 6.9 Hz, 1H, C$\underline{H}$Me$_2$), 2.50-2.35 (m, 2H, $H_{6endo/7endo}$), 1.54 (s, 9H, t-Bu

), 1.27 (d, *J* = 6.9 Hz, 6H, CH$\underline{\text{Me}}_2$), 1.22-1.15 (m, 2H, $H_{6exo/7exo}$); $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) δ 5.55 ($H_{2/4}$ and $Cp^i$) ↔ δ 5.25 ($H_{1/5}$ and $Cp^i$); δ 5.25 ($H_{1/5}$ and $Cp^i$) ↔ δ 2.42 ($H_{6endo/7endo}$), δ 1.19 ($H_{6exo/7exo}$); δ 2.75 (C$\underline{\text{H}}$Me$_2$) ↔ δ 1.27 (CH$\underline{\text{Me}}_2$); δ 2.42 ($H_{6endo,7endo}$) ↔ δ 1.19 ($H_{6exo,7exo}$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 133.0 (s, $Cp^i$ ring quaternary), 89.3 (d, $^1J_{CH}$ = 168 Hz, $C_{2/4}$), 86.8 (d, $^1J_{CH}$ = 161 Hz, $C_{1/5}$), 85.0 (d, $^1J_{CH}$ = 188 Hz, $Cp^i$), 84.3 (d, $^1J_{CH}$ = 185 Hz, $Cp^i$), 35.5 (s, *t*-Bu quaternary), 33.8 (t, $^1J_{CH}$ = 134 Hz, $C_{6/7}$), 31.2 (q, $^1J_{CH}$ = 123 Hz, *t*-Bu), 27.1 (d, $^1J_{CH}$ = 121 Hz, $\underline{\text{C}}$HMe$_2$), 22.7 (q, $^1J_{CH}$ = 121 Hz, CH$\underline{\text{Me}}_2$); HMQC (300 MHz, $CDCl_3$) δ 89.3 ($C_{2/4}$) ↔ δ 5.53 ($H_{2/4}$); δ 86.8 ($C_{1/5}$) ↔ δ 5.24 ($H_{1/5}$); δ 85.0 ($Cp^i$) ↔ δ 5.24 ($Cp^i$); δ 84.3 ($Cp^i$) ↔ δ 5.57 ($Cp^i$); δ 33.8 ($C_{6/7}$) ↔ δ 2.42 ($H_{6endo/7endo}$), δ 1.19 ($H_{6exo/7exo}$); δ 31.2 (*t*-Bu) ↔ δ 1.54 (*t*-Bu); δ 27.1 ($\underline{\text{C}}$HMe$_2$) ↔ δ 2.75 (C$\underline{\text{H}}$Me$_2$); δ 22.7 (CH$\underline{\text{Me}}_2$) ↔ δ 1.27 (CH$\underline{\text{Me}}_2$). Analysis calculated for $C_{19}H_{27}BCoF_4$: C, 56.89; H, 6.78; found: C, 56.545; H, 6.839.



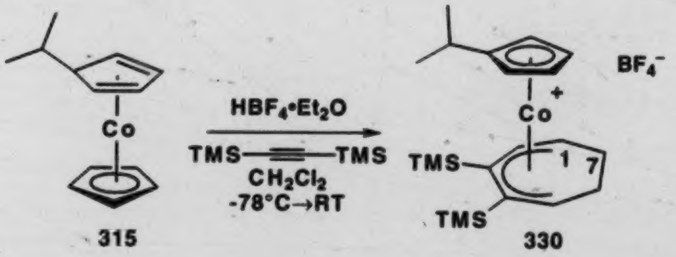
**$[(C_5H_4{}^iPr)Co(\eta^5\text{-}3\text{-}t\text{-}Bu\text{-}4\text{-}MeC_7H_7)]^+ BF_4^-$ (328).** In the drybox, a flask was charged with ($\eta^5$-$C_5H_5$)Co($\eta^4$-1-$^i$PrC$_5$H$_5$) (**315**) (0.1346 g, 0.5496 mmol) and removed to the Schlenk line, where dichloromethane (13 mL) was added. The solution was cooled to -78 °C and $HBF_4{\bullet}Et_2O$ (0.188 mL, 2.2 equiv) was added, turning the solution a deep red color. Upon addition of 3,3-dimethyl-2-pentyne (0.155 mL, 2 equiv), the color turned to green. After 1 h at -78 °C, the solution had turned a deep red color. Allowing the solution to warm to room temperature did not result in any further color change. Removal of all volatile material gave a dark oily residue. The compound was purified by flash chromatography (silica gel) using 5% methanol-dichloromethane. After a red band was collected and the solvent was removed, there remained an orange residue (0.0784 g, 33%). IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3112 (m), 2967 (s), 2875 (m), 1480 (s), 1401 (m), 1384 (m), 1369 (m), 1310 (w), 1283 (w), 1241 (w), 1172 (w), 1054 (s), 918 (w), 859 (m), 694 (w), 520 (m); $^1$H NMR (360 MHz, $CDCl_3$) δ 5.49 (br s, 1H, $Cp^i$), 5.40 (br s, 1H, $Cp^i$), 5.34[a] (br d, $J_{1\text{-}2}$ = 9.5 Hz, 1H, $H_1$), 5.26[b] (d, $J_{2\text{-}1}$ = 9.6 Hz, 1H, $H_2$), 5.24 (br s, 1H, $Cp^i$), 5.00 (br s, 1H, $Cp^i$), 4.97 (dd, $J_{5\text{-}6endo}$ = 8.4 Hz, $J_{5\text{-}6exo}$ = 5.0 Hz, 1H, $H_5$), 2.89 (dddd, $J_{7endo\text{-}7exo}$ = 17.1 Hz, $J_{7endo\text{-}6exo}$ = 11.2 Hz, $J_{7endo\text{-}6endo}$ = 8.7 Hz, $J_{7endo\text{-}1}$ = 3.6 Hz, 1H, $H_{7endo}$), 2.84 (septet, $J$ = 6.9 Hz, 1H, $C\underline{H}Me_2$), 2.42 (s, 3H, $Me_4$), 1.98 (br dd, $J_{7exo\text{-}7endo}$ = 17.3 Hz, $J_{7exo\text{-}6exo}$ = 6.2 Hz, $J_{7exo\text{-}1}$ = small, 1H, $H_{7exo}$), 1.71 (m, dddd by decoupling, $J_{6endo\text{-}6exo}$ = 13.6 Hz, $J_{6endo\text{-}5}$ = $J_{6endo\text{-}7endo}$ = 8.1 Hz, $J_{6endo\text{-}7exo}$ = small, 1H, $H_{6endo}$), 1.62 (s, 9H, *t*-Bu), 1.33 (d, $J$ = 7.2 Hz, 3H, $CH\underline{Me_2}$), 1.31 (d, $J$ = 7.2 Hz, 3H, $CH\underline{Me_2}$), 0.14 (m, dddd by decoupling, $J_{6exo\text{-}6endo}$ = $J_{6exo\text{-}7endo}$ = 11.5 Hz, $J_{6exo\text{-}7exo}$ = 6.1 Hz, $J_{6exo\text{-}5}$ = 5.6 Hz, 1H, $H_{6exo}$). [a] Several small unresolved couplings are noticed upon various decoupling experiments. [b] Signal overlaps with δ 5.24 signal. $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) δ 5.49 ($Cp^i$) ↔ δ 5.40 ($Cp^i$), δ 5.24 ($Cp^i$), δ 5.00 ($Cp^i$); δ 5.40 ($Cp^i$) ↔ δ 5.24 ($Cp^i$), δ 5.00 ($Cp^i$); δ 5.34 ($H_1$) ↔ δ 5.26 ($H_2$), δ 2.89 ($H_{7endo}$), δ 1.98 ($H_{7exo}$); δ 5.24 ($Cp^i$) ↔ δ 5.00 ($Cp^i$); δ 5.26 ($H_2$) ↔ δ 2.42 (w, $Me_4$), δ 1.98 ($H_{7exo}$); δ 4.97 ($H_5$) ↔ δ 2.42 (w, $Me_4$), δ 1.71 ($H_{6endo}$), δ 0.14 ($H_{6exo}$); δ 2.89 ($H_{7endo}$) ↔ δ 1.98 ($H_{7exo}$), δ 1.71 ($H_{6endo}$), δ 0.14 ($H_{6exo}$); δ 2.84 ($C\underline{H}Me_2$) ↔ δ 1.33 ($CH\underline{Me_2}$), δ 1.31 ($CH\underline{Me_2}$); δ 1.98 ($H_{7exo}$) ↔ δ 1.71 ($H_{6endo}$), δ 0.14 ($H_{6exo}$); δ 1.98 ($H_{7exo}$) ↔ δ 1.71[a] ($H_{6endo}$), δ 0.14 ($H_{6exo}$); δ 1.71 ($H_{7exo}$) ↔ δ 0.14 ($H_{6exo}$). [a]Extremely weak correlation; almost nonexistant. $^{13}$C NMR (100 MHz, $CDCl_3$, $^1J_{CH}$ values from HMQC spectrum) δ 135.1 (s, quaternary), 117.7 (s, quaternary), 115.0 (s, quaternary), 89.9 (d, $^1J_{CH}$ = 168 Hz, $C_2$), 87.1 (d, $^1J_{CH}$ = 186 Hz, $Cp^i$), 86.8 (d, $^1J_{CH}$ = 159 Hz, $C_5$), 86.7[a] ($C_1$), 86.2 (d, $^1J_{CH}$ = 183 Hz, $Cp^i$), 85.7 (d, $^1J_{CH}$ = 183 Hz, $Cp^i$), 84.6 (d, $^1J_{CH}$ = 181 Hz, $Cp^i$), δ 41.0 (t, $^1J_{CH}$ = 126 Hz, $C_7$), 36.6 (s, *t*-Bu quaternary), 32.3 (d, $^1J_{CH}$ = 128 Hz, *t*-Bu), 27.1 (q, $^1J_{CH}$ = 128 Hz, $\underline{C}HMe_2$), 25.61[b] (q, $^1J_{CH}$ = 128 Hz, $Me_4$), 25.58[b] (t, $^1J_{CH}$

= 128 Hz, $C_6$), 23.0 (q, $^1J_{CH}$ = 128 Hz, $CH\underline{Me_2}$), 22.6 (q, $^1J_{CH}$ = 128 Hz, $CH\underline{Me_2}$). [a] Signal is unresolved in the HMQC spectrum. [b]Signals are not resolved in the HMQC spectrum. HMQC (300 MHz, $CDCl_3$) δ 89.9 ($C_2$) ↔ δ 5.26 ($H_2$); δ 87.1 ($Cp^i$) ↔ δ 5.24 ($Cp^i$); δ 86.8 ($C_5$) ↔ δ 4.97 ($H_5$); δ 86.7[a] ($C_1$) ↔ δ 5.34 ($H_1$); δ 86.2 ($Cp^i$) ↔ δ 5.00 ($Cp^i$); δ 85.7 ($Cp^i$) ↔ δ 5.40 ($Cp^i$); δ 84.6 ($Cp^i$) ↔ δ 5.49 ($Cp^i$); δ 41.0 ($C_7$) ↔ δ 2.89 ($H_{7endo}$), δ 1.98 ($H_{7exo}$); δ 32.3 (*t*-Bu) ↔ δ 1.62 (*t*-Bu); δ 27.1 ($\underline{C}HMe_2$) ↔ δ 2.84 ($C\underline{H}Me_2$); δ 25.61 ($Me_4$) ↔ δ 2.42 ($Me_4$); δ 25.58 ($C_6$) ↔ δ 1.71 ($H_{6endo}$), δ 0.14 ($H_{6exo}$); δ 23.0 ($CH\underline{Me_2}$) ↔ δ 1.33 ($CH\underline{Me_2}$); δ 22.6 ($CH\underline{Me_2}$) ↔ δ 1.31 ($CH\underline{Me_2}$). [a] Signal is not totally resolved, but is assigned here. Analysis calculated for $C_{20}H_{29}BCoF_4$: C, 57.86; H, 7.04; found: C, 57.435; H, 7.387.



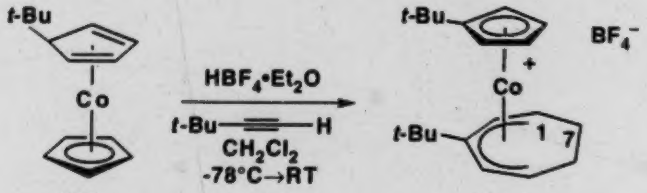
**$[(C_5H_4{}^iPr)Co(\eta^5\text{-}4\text{-}Me\text{-}3\text{-}(SiMe_3)C_7H_7)]^+ BF_4^-$ (329).** In the drybox, a flask was charged with ($\eta^5$-$C_5H_5$)Co($\eta^4$-1-$^i$Pr$C_5H_5$) (**315**) (0.1246 g, 0.5366 mmol) and removed to the Schlenk line, where dichloromethane (12 mL) was added. The solution was cooled to -78 °C and $HBF_4$•$Et_2O$ (0.17 mL, 2.2 equiv) was added, turning the solution a deep red color. Upon addition of 1-(trimethylsilyl)propyne (0.16 mL, 2 equiv), the color slowly turned to green. After 2 h at -78 °C, the solution had turned a deep red color. Allowing the solution to warm to room temperature did not result in any further color change. Removal of all volatile material gave a dark oily residue. The compound was purified by flash chromatography (silica gel) using 5% methanol-dichloromethane. After a red band was collected and the solvent was removed, there remained a red residue (0.0444 g, 21%). IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3111 (w), 2964 (m), 1479 (m), 1435 (m), 1384 (m), 1311 (w), 1256 (s), 1054 (s), 979 (m), 922 (m), 839 (s), 762 (m), 723 (w), 696 (w), 622 (w), 520 (m); $^1$H NMR (360 MHz, $CDCl_3$) δ 5.60-5.50 (m, $J_{1\text{-}2}$ = 9.3 Hz, 1H, $H_1$), 5.52-5.48 (m, 1H, $Cp^i$), 5.44-5.38 (m, 2H, $Cp^i$), 5.17 (d, $J_{2\text{-}1}$ = 9.6 Hz, 1H, $H_2$), 5.06-5.03 (m, 1H, $Cp^i$), 4.96 (dd, $J_{5\text{-}6endo}$ = 8.4 Hz, $J_{5\text{-}6exo}$ = 5.1 Hz, 1H, $H_5$), 2.95 (m, dddd by decoupling, $J_{7endo\text{-}7exo}$ = 17.4 Hz, $J_{7endo\text{-}6exo}$ = 11.0 Hz, $J_{7endo\text{-}6endo}$ = 9.0 Hz, $J_{7endo\text{-}1}$ = 3.9 Hz, 1H, $H_{7endo}$), 2.65 (septet, $J$ = 6.9 Hz, 1H, $C\underline{H}Me_2$), 2.57 (s, 3H, $Me_4$), 2.03 (br d, $J$ = 17.4 Hz, ddd by decoupling, $J_{7exo\text{-}7endo}$ = 17.2 Hz, $J_{7exo\text{-}6exo}$ = 5.7 Hz, $J_{7exo\text{-}1}$ ≈ 2 Hz, 1H, $H_{7exo}$), 1.79 (m, dddd by decoupling, $J_{6endo\text{-}6exo}$ = 12.6 Hz, $J_{6endo\text{-}7endo}$ = $J_{6endo\text{-}5}$ = 8.2 Hz, $J_{6endo\text{-}1}$ = small, 1H, $H_{6endo}$), 1.28 (d, $J$ = 7.0 Hz, 3H, $CH\underline{Me_2}$), 1.26 (d, $J$ = 7.0 Hz, 3H, $CH\underline{Me_2}$), 0.41 (s, 9H, $SiMe_3$), 0.24 (m, dddd by decoupling, $J_{6exo\text{-}6endo}$ = $J_{6exo\text{-}7endo}$ = 11.1 Hz, $J_{6exo\text{-}7exo}$ = 6.0 Hz, $J_{6exo\text{-}5}$ = 5.1 Hz, 1H, $H_{6exo}$); $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) δ 5.55 ($H_1$) ↔ δ 5.17 ($H_2$), δ 2.95 ($H_{7endo}$), δ 2.03 ($H_{6endo}$), δ 1.79 ($H_{6endo}$); δ 5.50 ($Cp^i$) ↔ δ 5.41 ($Cp^i$), δ 5.04 ($Cp^i$); δ 5.41 ($Cp^i$) ↔ δ 5.04 ($Cp^i$); δ 5.17 ($H_2$) ↔ δ 2.57 (w, $Me_4$), δ 2.03 ($H_{7exo}$); δ 4.96 ($H_5$) ↔ δ 2.57 (w, $Me_4$), δ 1.79 ($H_{6endo}$), δ 0.24 ($H_{6exo}$); δ 2.95 ($H_{7endo}$) ↔ δ 2.03 ($H_{7exo}$), δ 1.79 ($H_{6endo}$), δ 0.24 ($H_{6exo}$); δ 2.65 ($C\underline{H}Me_2$) ↔ δ 1.28 ($CH\underline{Me_2}$), δ 1.26 ($CH\underline{Me_2}$); δ 2.03 ($H_{7exo}$) ↔ δ 1.79$^a$ (vw, $H_{6endo}$), δ 0.24 ($H_{6exo}$); δ 1.79 ($H_{6endo}$) ↔ δ 0.24 ($H_{6exo}$). $^a$Only a very weak correlation is seen. $^{13}$C NMR (100 MHz, $CDCl_3$ $^1J_{CH}$ obtained from HMQC spectrum) δ 121.7 (s, $C_3$), 115.5 (s, $Cp^i$ ring quaternary), 101.7 (s, $\underline{C_4}$), 95.5 (d, $^1J_{CH}$ = 166 Hz, $C_2$), 91.1 (d, $^1J_{CH}$ = 155 Hz, $C_1$), 88.9 (d, $^1J_{CH}$ = 159 Hz, $C_5$), 86.1 (d, $^1J_{CH}$ = 184 Hz, $Cp^i$), 85.1 (d, $^1J_{CH}$ = 184 Hz, $Cp^i$), 84.7 (d, $^1J_{CH}$ = 182 Hz, $Cp^i$), 84.5 (d, $^1J_{CH}$ = 182 Hz, $Cp^i$), 41.7 (t, $^1J_{CH}$ = 124 Hz, $C_7$), 27.3 (t, $^1J_{CH}$ = 131 Hz, $C_6$), 27.0 (d, $^1J_{CH}$ = 129 Hz, $\underline{C}HMe_2$), 23.3 (q, $^1J_{CH}$ = 126 Hz, $CH\underline{Me_2}$), 23.0 (q, $^1J_{CH}$ = 127 Hz, $Me_4$), 22.2 (q, $^1J_{CH}$ = 129 Hz, $CH\underline{Me_2}$), 0.045 (q, $^1J_{CH}$ = 117 Hz, $Si\underline{Me_3}$); HMQC (300 MHz, $CDCl_3$) δ 95.5 ($C_2$) ↔ δ 5.17 ($H_2$); δ 91.1 ($C_1$) ↔ δ 5.55 ($H_1$); δ 88.9 ($C_5$) ↔ δ 4.96 ($H_5$); δ 86.1 ($Cp^i$) ↔ δ 5.41 ($Cp^i$); δ 85.1 ($Cp^i$) ↔ δ 5.04 ($Cp^i$); δ 84.7 ($Cp^i$) ↔ δ 5.41 ($Cp^i$); δ 84.5 ($Cp^i$) ↔ δ 5.50 ($Cp^i$); δ 41.7 ($C_7$) ↔ δ 2.95 ($H_{7endo}$), δ 2.03 ($H_{7exo}$); δ 27.3 ($C_6$) ↔ δ 1.79 ($H_{6endo}$), δ 0.24

$(H_{6exo})$; δ 27.0 $(\underline{C}HMe_2)$ ↔ δ 2.65 $(C\underline{H}Me_2)$; δ 23.3 $(CH\underline{Me_2})$ ↔ δ 1.26 $(CH\underline{Me_2})$; δ 23.0 $(Me_4)$ ↔ δ 2.57 $(Me_4)$; δ 22.2 $(CH\underline{Me_2})$ ↔ δ 1.28 $(CH\underline{Me_2})$; δ 0.045 $(Si\underline{Me_3})$ ↔ δ 0.41 $(Si\underline{Me_3})$; HMBC (300 MHz, $CDCl_3$) δ 121.7 $(C_3)$ ↔ δ 4.96 $(H_5)$, δ 2.57 $(Me_4)$; δ 115.5 $(Cp^i)$ ↔ δ 5.50 $(Cp^i)$, δ 5.41 $(Cp^i)$, δ 5.04 $(Cp^i)$, δ 2.65 $(C\underline{H}Me_2)$, δ 1.28 $(CH\underline{Me_2})$, δ 1.26 $(CH\underline{Me_2})$; δ 101.77 $(C_4)$ ↔ δ 5.17 $(H_2)$, δ 4.96 $(H_5)$, δ 2.57 $(Me_4)$, δ 1.79 $(H_{6endo})$, δ 0.24 $(H_{6exo})$; δ 95.5 $(C_2)$ ↔ δ 2.95 $(H_{7endo})$, δ 2.57 $(Me_4)$; δ 91.1 $(C_1)$ ↔ δ 2.95 $(H_{7endo})$, δ 2.03 $(H_{7exo})$, δ 1.79 $(H_{6endo})$; δ 88.9 $(C_5)$ ↔ δ 2.03 $(H_{7exo})$, δ 1.79 $(H_{6endo})$, δ 0.24 $(H_{6exo})$; δ 86.1/ 85.1/ 84.7/ 84.5[a] $(Cp^i)$ ↔ δ 5.50 $(Cp^i)$, δ 5.41 $(Cp^i)$, δ 5.04 $(Cp^i)$, δ 2.65 $(C\underline{H}Me_2)$; δ 41.7 $(C_7)$ ↔ δ 5.17 $(H_2)$, δ 4.96 $(H_5)$, δ 1.79 $(H_{6endo})$, δ 0.24 $(H_{6exo})$; δ 27.3 $(C_6)$ ↔ δ 4.96 $(H_5)$, δ 2.95 $(H_{7endo})$; δ 27.0 $(\underline{C}HMe_2)$ ↔ δ 1.28 $(CH\underline{Me_2})$; δ 23[b] $(Me_4$ and $CH\underline{Me_2})$ ↔ δ 5.17 $(H_2)$, δ 2.65 $(C\underline{H}Me_2)$, δ 1.26 $(CH\underline{Me_2})$; δ 22.2 $(CH\underline{Me_2})$ ↔ δ 2.65 $(C\underline{H}Me_2)$, δ 1.28 $(CH\underline{Me_2})$, δ 1.26 $(CH\underline{Me_2})$. [a] Signals are not resolved: one large correlation is seen for all carbon signals. [b]Signals at δ 23.3 $(CH\underline{Me_2})$ and δ 23.0 $(Me_4)$ are not resolved. Analysis calculated for $C_{19}H_{29}BCoF_4Si$: C, 52.92; H, 6.78; found: C, 52.787; H, 6.924.



**$[(C_5H_4{}^iPr)Co(\eta^5\text{-}3,4\text{-}(SiMe_3)_2C_7H_7)]^+\ BF_4^-$ (330).** In the drybox, a flask was charged with $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}1\text{-}{}^iPrC_5H_5)$ **(315)** (0.1622 g, 0.6985 mmol) and removed to the Schlenk line, where dichloromethane (10 mL) was added. The solution was cooled to -78 °C and bis(trimethylsilyl)acetylene (0.30 mL, 2.0 equiv) and $HBF_4•Et_2O$ (0.25 mL, 2.2 equiv) were added, turning the solution a deep red color. Allowing the solution to warm to room temperature did not result in any further color change. Removal of all volatile material gave a dark oily residue. The compound was purified by flash chromatography (silica gel) using 5% methanol-dichloromethane. After a red band was collected and the solvent was removed, there remained a solid red residue (0.1451 g, 48%). IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3111 (m), 2962 (s), 1480 (m), 1459 (m), 1432 (m), 1414 (m), 1367 (w), 1341 (w), 1310 (w), 1254 (s), 1054 (s), 980 (m), 866 (s), 835 (s), 759 (s), 733 (m), 699 (m), 638 (m), 628 (w), 521 (m); $^1$H NMR (360 MHz, $CDCl_3$) δ 5.72 (br d, $J_{1\text{-}2}$ = 8.8 Hz, 1H, $H_1$), 5.64 (br s, 1H, Cp$^i$), 5.45 (br s, 1H, Cp$^i$), 5.20-5.15 (m, 3H, Cp$^i$, $H_2$, $H_5$), 4.95 (br s, 1H, Cp$^i$), 3.04 (m, dddd by decoupling, $J_{\text{7exo-7endo}}$ = 17.9 Hz, $J_{\text{7endo-6exo}}$ = 11.6 Hz, $J_{\text{7endo-6endo}}$ = 8.5 Hz, $J_{\text{7endo-1}}$ = 3.4 Hz, 1H, $H_{\text{7endo}}$), 2.85 (septet, $J$ = 6.8 Hz, 1H, C$\underline{\mathrm{H}}$Me$_2$), 2.14 (br d, $J_{\text{obs}}$ = 14.4 Hz, dddd by decoupling, $J_{\text{7exo-7endo}}$ = 17.8 Hz, $J_{\text{7exo-6exo}}$ = 5.5 Hz, $J_{\text{7exo-1}}$ = 2.9 Hz, $J_{7\text{-}2}$ = small, 1H, $H_{\text{7exo}}$), 1.70 (m, ddddd by decoupling, $J_{\text{6endo-6exo}}$ = 12.0 Hz, $J_{\text{6endo-7endo}}$ = $J_{\text{6endo-5}}$ = 8.2 Hz, $J_{\text{6endo-1}}$ = small, $J_{\text{6endo-7exo}}$ = very small, 1H, $H_{\text{6endo}}$), 1.33 (d, $J$ = 6.9 Hz, 6H, CH$\underline{\mathrm{Me}_2}$)0.53 (s, 9H, Si$\underline{\mathrm{Me}_3}$), 0.40 (s, 9H, Si$\underline{\mathrm{Me}_3}$), 0.075 (m, dddd by decoupling, $J_{\text{6exo-6endo}}$ = $J_{\text{6exo-7endo}}$ = 11.9 Hz, $J_{\text{6exo-7exo}}$ = 5.5 Hz, $J_{\text{6exo-5}}$ = 5.3 Hz, 1H, $H_{\text{6exo}}$). $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) δ 5.72 ($H_1$) $\leftrightarrow$ δ 5.17 ($H_2$), δ 3.04 ($H_{\text{7endo}}$), δ 2.14 ($H_{\text{7exo}}$), δ 1.70 (w, $H_{\text{6endo}}$); δ 5.64 (Cp$^i$) $\leftrightarrow$ δ 5.45 (Cp$^i$), δ 5.17 (Cp$^i$), δ 4.95 (Cp$^i$), δ 2.85 (w, CHMe$_2$); δ 5.45 (Cp$^i$) $\leftrightarrow$ δ 5.17 (Cp$^i$), δ 4.95 (Cp$^i$); δ 5.17 (Cp$^i$, $H_2$, $H_5$) $\leftrightarrow$ δ 4.95 (Cp$^i$), δ 2.14 (w, $H_{\text{7exo}}$), δ 1.70 ($H_{\text{6endo}}$), δ 0.075 ($H_{\text{6exo}}$); δ 3.04 ($H_{\text{7endo}}$) $\leftrightarrow$ δ 2.14 ($H_{\text{7exo}}$), δ 1.70 ($H_{\text{6endo}}$), δ 0.075 ($H_{\text{6exo}}$); δ 2.85 (C$\underline{\mathrm{H}}$Me$_2$) $\leftrightarrow$ δ 1.33 (CH$\underline{\mathrm{Me}_2}$); δ 2.14[a] ($H_{\text{7exo}}$) $\leftrightarrow$ δ 0.075 ($H_{\text{6exo}}$); δ 1.70 ($H_{\text{6endo}}$) $\leftrightarrow$ δ 0.075 ($H_{\text{6exo}}$). [a]There is no noticeable crosspeak between $H_{\text{7exo}}$ and $H_{\text{6endo}}$. $^{13}$C NMR (75 MHz, $CDCl_3$, $J$ values from HMQC spectrum) δ 120.2 (s, $C_{\text{quaternary}}$), 115.8 (s, $C_{\text{quaternary}}$), 107.2 (s, $C_{\text{quaternary}}$), 98.6 (d, $^1J_{CH}$ = 166 Hz, $C_2$), 93.9 (d, $^1J_{CH}$ = 157 Hz, $C_1$), 91.4 (d, $^1J_{CH}$ = 158 Hz, $C_5$), 85.6 (d, $^1J_{CH}$ = 186 Hz, Cp$^i$), 85.2 (d, $^1J_{CH}$ = 183 Hz, Cp$^i$), 84.07 (d, $^1J_{CH}$ = 186 Hz, Cp$^i$), 83.98 (d, $^1J_{CH}$ = 184 Hz, Cp$^i$), 42.3 (t, $^1J_{CH}$ = 126 Hz, $C_7$), 27.3 (d, $^1J_{CH}$ = 134 Hz, $\underline{\mathrm{C}}$HMe$_2$), 26.7 (t, $^1J_{CH}$ = 132 Hz, $C_6$), 23.2[a] (q, $^1J_{CH}$ = 124 Hz, CH$\underline{\mathrm{Me}_2}$), 22.4[a] (q, $^1J_{CH}$ = 124 Hz, CH$\underline{\mathrm{Me}_2}$), 2.1 (q, $^1J_{CH}$ = 118 Hz, Si$\underline{\mathrm{Me}_3}$), 1.5

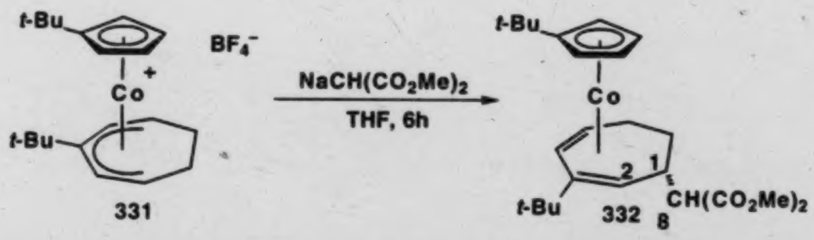
(q, ${}^1J_{CH}$ = 118 Hz, Si$\underline{\mathrm{Me}}_3$). ${}^a$These carbons are not resolved. HMQC (300 MHz, $CDCl_3$) δ 98.6 ($C_2$) ↔ δ 5.17 ($H_2$); δ 93.9 ($C_1$) ↔ δ 5.72 ($H_1$); δ 91.4 ($C_5$) ↔ δ 5.17 ($H_5$); δ 85.6 ($C_p{}^i$) ↔ δ 5.64 ($Cp^i$); δ 85.2 ($Cp^i$) ↔ δ 5.17 ($Cp^i$); δ 84.07 ($Cp^i$) ↔ δ 5.45 ($Cp^i$); δ 83.98 ($Cp^i$) ↔ δ 4.95 ($Cp^i$); δ 42.3 ($C_7$) ↔ δ 3.04 ($H_{7endo}$), δ 2.14 ($H_{7endo}$); δ 27.3 ($\underline{\mathrm{C}}HMe_2$) ↔ δ 2.85 ($C\underline{\mathrm{H}}Me_2$); δ 26.7 ($C_6$) ↔ δ 1.70 ($H_{6endo}$), δ 0.075 ($H_{6endo}$); δ 23.2${}^a$ ($CH\underline{\mathrm{Me}}_2$) ↔ δ 1.33 ($CH\underline{\mathrm{Me}}_2$); δ 22.4${}^a$ ($CH\underline{\mathrm{Me}}_2$) ↔ δ 1.33 ($CH\underline{\mathrm{Me}}_2$); δ 2.1 ($Si\underline{\mathrm{Me}}_3$) ↔ δ 0.53 ($Si\underline{\mathrm{Me}}_3$); δ 1.5 ($Si\underline{\mathrm{Me}}_3$) ↔ δ 0.40 ($Si\underline{\mathrm{Me}}_3$). ${}^a$These carbons are not resolved. Analysis calculated for $C_{21}H_{36}BCoF_4Si_2$: C, 51.42; H, 7.41; found: C, 51.133; H, 7.460.



316 331

**[($C_5H_4$*t*-Bu)Co($\eta^5$-3-*t*-Bu-$C_7H_8$)]$^+$ $BF_4^-$ (331).** In the drybox, ($\eta^5$-$C_5H_5$)Co($\eta^4$-1-*t*-Bu-$C_5H_5$) **(316)** (0.1005 g, 0.4081 mmol) was weighed into a Schlenk flask. The compound was dissolved in degassed dichloromethane (10 mL) and cooled to -78 °C. To the solution was added 3,3-dimethyl-1-butyne (0.50 mL, 10 equiv), followed by $HBF_4$•$Et_2O$ (0.13 mL, 2.2 equiv). The color of the red solution deepened immediately upon addition of the acid. The solution was slowly warmed with stirring over a 12 h period. Removal of the solvent was followed by flash chromatography on silica gel using 5% methanol/dichloromethane. Crystallization from dichloromethane/diethyl ether gave a light orange powder (112 mg, 66%). IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3113 (m), 2964 (m), 2910 (w), 2874 (w), 1497 (w), 1484 (w), 1467 (w), 1409 (w), 1398 (w), 1392 (w), 1372 (w), 1280 (w), 1151 (w), 1055 (s), 1035 (s), 904 (w), 857 (w), 837 (w); ${}^1H$ NMR (300 MHz, $CDCl_3$) δ 5.57 (d, $J_{2\text{-}1}$ = 8.9 Hz, 2H, $H_{2/4}$), 5.52 (t, *J* = 2.2 Hz, 2H, $Cp^t$), 5.4-5.3 (m, 2H, $H_{1/5}$), 5.21 (t, *J* = 2.2 Hz, 2H, $Cp^t$), 2.5-2.3 (m, 2H, $H_{6endo/7endo}$), 1.52 (s, 9H, *t*-Bu), 1.33 (s, 9H, *t*-Bu), 1.2-1.1 (m, 2H, $H_{6exo/7exo}$); ${}^1H$-${}^1H$ GCOSY (300 MHz, $CDCl_3$) δ 5.57

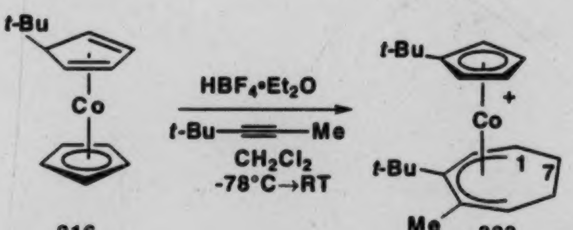
($H_{2/4}$) ↔ δ 5.35 ($H_{1/5}$); δ 5.52 ($Cp^t$) ↔ δ 5.21 ($Cp^t$); δ 5.35 ($H_{1/5}$) ↔ δ 2.4 ($H_{6endo/7endo}$), δ 1.15 ($H_{6exo/7exo}$); δ 2.4 ($H_{6endo/7endo}$) ↔ δ 1.15 ($H_{6exo/7exo}$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 134.2 (s, $C_3$), 121.2 (s, Cp' ring quaternary), 90.0 (d, $^1J_{CH}$ = 166.5 Hz, $C_{2/4}$), 85.4 (d, $^1J_{CH}$ = 156.6 Hz, $C_{1/5}$), 84.2[a] (d, $^1J_{CH}$ = 181.5 Hz, $Cp^t$), 84.0[a] (d, $^1J_{CH}$ = 181.5 Hz, $Cp^t$), 36.1 (s, *t*-Bu, quaternary), 34.1 (d, $^1J_{CH}$ = 132.6 Hz, $C_{6/7}$), 31.8 (s, *t*-Bu quaternary), 31.1 (q, $^1J_{CH}$ = 127.3 Hz, *t*-Bu), 30.7 (q, $^1J_{CH}$ = 126.3 Hz, *t*-Bu). [a] These carbons overlap in the $^1H$ coupled spectrum. *J* values are approximate. $^1H$-$^{13}C$ HETCORR (100 MHz, $CDCl_3$) δ 90.0 ($C_{2/4}$) ↔ δ 5.57 ($H_{2/4}$); δ 85.4 ($C_{1/5}$) ↔ δ 5.35 ($H_{1/5}$); δ 84.2 ($Cp^t$) ↔ δ 5.21 ($Cp^t$); δ 84.0 ($Cp^t$) ↔ δ 5.52 ($Cp^t$); δ 34.1 ($C_{6/7}$) ↔ δ 2.4 ($H_{6endo/7endo}$), δ 1.15 ($H_{6exo/7exo}$); δ 31.1 (*t*-Bu) ↔ δ 1.52 (*t*-Bu); δ 30.7 (*t*-Bu) ↔ δ 1.33 (*t*-Bu). Analysis calculated for $C_{20}H_{30}BCoF_4$: C, 57.72; H, 7.27; found: C, 57.467; H, 7.021.



**1-*t*-Butyl-cyclopentadienyl[dimethyl (2-5-η-3-*t*-butyl-cyclohepta-2,4-dienyl)-malonate]cobalt. [($\eta^5$-1-*t*-Bu-$C_5H_4$)Co($\eta^4$-3-*t*-Bu-1-(bis(carbomethoxy)methyl)-$C_7H_8$)] (332)**. In the drybox, [(*t*-BuCp)Co($\eta^5$-3-*t*-Bu-$C_7H_8$)]$^+$ $BF_4^-$ **(331)** (55.2 mg, 0.133 mmol) was placed in a Schlenk flask and tetrahydrofuran (15 mL) was added to form an orange-red slurry. Sodium dimethylmalonate (27.6 mg, 0.179 mmol, 1.4 equiv) was added. The slurry slowly dissolved and the solution turned deep red. The reaction was stirred for 6 h, then all volatiles were removed *in vacuo*. The residue was extracted with pentane and the pentane extracts were combined and filtered through a pad of Celite. The solvent was removed, leaving a deep red oil (48.8 mg, 80%). IR (hexane cast, $cm^{-1}$) 2957 (s), 2905 (m), 2868 (m), 1759 (s), 1735 (s), 1481 (w), 1456 (w), 1433 (m), 1391

(w), 1362 (m), 1359 (m), 1325 (m), 1294 (w), 1261 (s), 1232 (m), 1200 (m), 1151 (s), 1132 (m), 1087 (s), 1059 (m), 1019 (s), 910 (w), 870 (w), 843 (w), 800 (s); $^1$H NMR (400 MHz, $C_6D_6$) δ 4.72-4.70 (m, 1H, $Cp^t$), 4.67-4.63 (m, 1H, $Cp^t$), 4.44-4.43 (m, 1H, $Cp^t$), 4.40 (d, $J_{obs}$ = 7 Hz, dd by decoupling, $J_{4\text{-}5}$ = 7.3 Hz, $J_{4\text{-}6exo}$ < 2 Hz, 1H, $H_4$), 3.85-3.83 (m, 1H, $Cp^t$), 3.39 (s, 3H, $CO_2Me$), 3.26 (d, $J_{8\text{-}1}$ = 10.5 Hz, 1H, $H_8$, overlaps with $CO_2Me$), 3.24 (s, 3H, $CO_2Me$), 3.05-3.04 (m, 1H, $H_2$), 2.96 (apparent t, $J_{obs}$ = 6.5 Hz, dddd by decoupling, $J_{5\text{-}4}$ = 7.3 Hz, $J_{5\text{-}6exo}$ = 5.8 Hz, $J_{5\text{-}6endo}$ < 2 Hz, $J_{5\text{-}7endo}$ = 1.7 Hz, 1H, $H_5$), 2.73 (m, dddd by decoupling, $J_{1\text{-}7exo}$ = 12.0 Hz, $J_{1\text{-}8}$ = 10.5 Hz, $J_{1\text{-}7endo}$ = 3.3 Hz, $J_{1\text{-}2}$ = 1.7 Hz, 1H, $H_1$), 1.67 (m, dddd by decoupling, $J_{6endo\text{-}6exo}$ = 16.8 Hz, $J_{6endo\text{-}7exo}$ = 12.9 Hz, $J_{6endo\text{-}7endo}$ = 3.5 Hz, $J_{6endo\text{-}5}$ = 1.8 Hz, 1H, $H_{6endo}$), 1.52 (m, dddd by decoupling, $J_{6exo\text{-}6endo}$ = 16.7 Hz, $J_{6exo\text{-}5}$ = 5.8 Hz, $J_{6exo\text{-}7exo}$ = 3.7 Hz, $J_{6exo\text{-}7endo}$ ≈ 3.7 Hz, 1H, $H_{6exo}$), 1.42 (m, dddd by decoupling, $J_{7endo\text{-}7exo}$ = 12.8 Hz, $J_{7endo\text{-}6exo}$ = 3.7 Hz, $J_{7endo\text{-}6endo}$ = 3.5 Hz, $J_{7endo\text{-}1}$ = 3.3 Hz, 1H, $H_{7endo}$), 1.26 (s, 9H, $Cp^t$ *t*-Bu), 1.24 (s, 9H, $C_3$ *t*-Bu), 0.48 (dddd, $J_{7exo\text{-}6endo}$ = 12.9 Hz, $J_{7exo\text{-}7endo}$ = 12.5 Hz, $J_{7exo\text{-}1}$ = 12.0 Hz, $J_{7exo\text{-}6exo}$ = 3.7 Hz, 1H, $H_{7exo}$); $^1$H-$^1$H GCOSY (300 MHz, $C_6D_6$) δ 4.72 ($Cp^t$) ↔ δ 4.44 ($Cp^t$), δ 3.85 ($Cp^t$); δ 4.67 ($Cp^t$) ↔ δ 4.44 ($Cp^t$), δ 3.85 ($Cp^t$); δ 4.44 ($Cp^t$) ↔ δ 3.85 ($Cp^t$); δ 4.40 ($H_4$) ↔ δ 2.96 ($H_5$), δ 1.52 (w, $H_{6exo}$); δ 3.26 ($H_8$) ↔ δ 2.73 ($H_1$); δ 3.05 ($H_2$) ↔ δ 2.73 ($H_1$), δ 1.42 (w, $H_{7endo}$); δ 2.96 ($H_5$) ↔ δ 1.67 ($H_{6endo}$), δ 1.52 ($H_{6exo}$); δ 2.73 ($H_1$) ↔ δ 1.42 ($H_{7endo}$), δ 0.48 ($H_{7exo}$); δ 1.67 ($H_{6endo}$) ↔ δ 1.52 ($H_{6exo}$), δ 1.42 ($H_{7endo}$), δ 0.48 ($H_{7exo}$); δ 1.52 ($H_{6exo}$) ↔ δ 1.42 ($H_{7endo}$), δ 0.48 ($H_{7exo}$); δ 1.42 ($H_{7endo}$) ↔ δ 0.48 ($H_{7exo}$); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 169.2 (s, $CO_2Me$), 168.1 (s, $CO_2Me$), 112.6 (s, $Cp^t$ ring quaternary), 108.1 (s, $C_3$), 80.5 (d, $^1J_{CH}$ = 173 Hz, $Cp^t$), 79.8 (d, $^1J_{CH}$ = 171.9 Hz, $Cp^t$), 78.9[a] (d, $^1J_{CH}$ = 164 Hz, $Cp^t$), 78.8[a] (d, $^1J_{CH}$ = 164 Hz, $Cp^t$), 75.8 (d, $^1J_{CH}$ = 161.6 Hz, $C_4$), 60.9 (d, $^1J_{CH}$ = 134.4 Hz, $C_8$), 51.7 (q, $^1J_{CH}$ = 147.0 Hz, $CO_2Me$), 51.6 (q, $^1J_{CH}$ = 147.2 Hz, $CO_2Me$), 45.5 (d, $^1J_{CH}$ = 143.5 Hz, $C_5$), 40.9 (d, $^1J_{CH}$ = 134.4 Hz, $C_1$), 39.8 (d, $^1J_{CH}$ = 143.8 Hz, $C_2$), 33.9 (s, $C_3$ *t*-Bu quaternary), 31.7[c] (q, $^1J_{CH}$ = 125.3 Hz, $Cp^t$ *t*-Bu), 31.4[c] (s, $Cp^t$ *t*-Bu quaternary), 30.6[c] (q, $^1J_{CH}$ = 125.0 Hz,

$C_3$ *t*-Bu ), 29.8$^c$ (t, $^1J_{CH}$ = 125.9 Hz, $C_6$), 27.3 (t, $^1J_{CH}$ = 125.1 Hz, $C_7$). $^{a, b,c}$ Denote pairs of overlaping signals in the gated decoupled spectrum: $^1J_{CH}$'s are approximate. HMQC (300 MHz, $C_6D_6$) δ 80.5 ($Cp^t$) ↔ δ 4.67 ($Cp^t$); δ 79.8 ($Cp^t$) ↔ δ 4.72 ($Cp^t$); δ 78.9/ 78.8 ($Cp^t$) ↔ δ 4.43 ($Cp^t$), δ 3.85 ($Cp^t$); δ 75.8 ($C_4$) ↔ δ 4.40 ($H_4$); δ 60.9 ($C_8$) ↔ δ 3.23 ($H_8$); δ 51.7 ($CO_2Me$) ↔ δ 3.39 ($CO_2Me$); δ 51.6 ($CO_2Me$) ↔ δ 3.24 ($CO_2Me$); δ 45.5 ($C_5$) ↔ δ 2.96 ($H_5$); δ 40.9 ($C_1$) ↔ δ 2.73 ($H_1$); δ 39.8 ($C_2$) ↔ δ 3.05 ($H_2$); δ 31.7 ($Cp^t$ *t*-Bu ) ↔ δ 1.26 ($Cp^t$ *t*-Bu); δ 30.6 ($C_3$ *t*-Bu ) ↔ δ 1.24 ($C_3$ *t*-Bu ); δ 29.8$^a$ ($C_6$) ↔ δ 1.67 ($H_{6endo}$), δ 1.52 ($H_{6exo}$); δ 27.3 ($C_7$) ↔ δ 1.42 ($H_{7endo}$), δ 0.48 ($H_{7exo}$). $^a$Signal is partially obscured by the *t*-Bu signal. HMBC (300 MHz, $C_6D_6$) δ 169.2 ($CO_2Me$) ↔ δ 3.39 ($CO_2Me$); δ 168.1 ($CO_2Me$) ↔ δ 3.24 ($CO_2Me$); δ 112.6 ($Cp^t$ ring quaternary$_5$) ↔ δ 4.72 ($Cp^t$), δ 4.67 ($Cp^t$), δ 4.44 ($Cp^t$), δ 3.85 ($Cp^t$), δ 1.26 ($Cp^t$ *t*-Bu quaternary); δ 108.1 ($C_3$) ↔ δ 2.96 ($H_5$), δ 2.73 ($H_1$), δ 1.24 ($C_3$ *t*-Bu); δ 80.5 ($Cp^t$) ↔ δ 4.72 ($Cp^t$), δ 4.44 ($Cp^t$), δ 3.85 ($Cp^t$); δ 79.8 ($Cp^t$) ↔ δ 4.67 ($Cp^t$), δ 3.85 ($Cp^t$); δ 78.9/ 78.8 ($Cp^t$) ↔ δ 4.72 ($Cp^t$), δ 4.67 ($Cp^t$), δ 4.44 ($Cp^t$), δ 3.85 ($Cp^t$); δ 75.8 ($C_4$) ↔ δ 3.05 ($H_2$); δ 60.9 ($C_8$) ↔ δ 3.05 ($H_2$), δ 2.73 ($H_1$); δ 45.5 ($C_5$) ↔ δ 0.48 (w, $H_{7exo}$); δ 40.9 ($C_1$) ↔ δ 0.48 ($H_{7exo}$); δ 39.8 ($C_2$) ↔ δ 4.40 ($H_4$), δ 2.73 ($H_1$); δ 33.9 ($C_3$ *t*-Bu quaternary) ↔ δ 3.05 ($H_2$); δ 31.7 ($C_4$) ↔ δ 1.26 ($C_3$ *t*-Bu); δ 30.6 ($C_3$ *t*-Bu quaternary) ↔ δ 1.24 ($C_3$ *t*-Bu); δ 29.8 ($C_6$) ↔ δ 4.40 ($H_4$), δ 0.48 ($H_{7exo}$); δ 27.3 ($C_7$) ↔ δ 3.05 ($H_2$), δ 2.96 ($H_5$). MS *m/z* calculated for $C_{25}H_{37}CoO_4$ ($M^+$): 460.20239; found: 460.20204 (54 %).

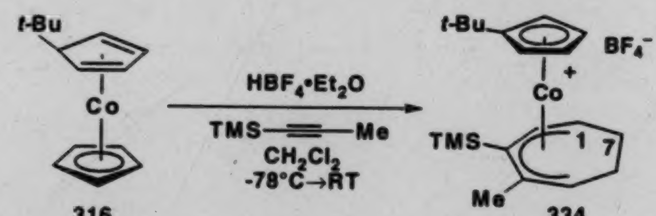


316 333

**[($C_5H_4$*t*-Bu)Co($\eta^5$-3-*t*-Bu-4-Me-$C_7H_8$)]$^+$ $BF_4^-$ (333).** A solution of CpCo($\eta^4$-1-*t*-Bu-$C_5H_5$) **(316)** (46.6 mg, 0.189 mmol) in dichloromethane (4 mL) was cooled to -78 °C. To the solution was added 4,4-dimethyl-2-pentyne (0.18 mL, 7 equiv), followed by

$HBF_4{\bullet}Et_2O$ (61.3 mL, 2.2 equiv). The color of the red solution deepened immediately upon addition of the acid. The solution was slowly warmed with stirring over a 12 h period. Removal of the solvent was followed by flash chromatography on silica gel using 5% methanol/dichloromethane. Recrystallization from dichloromethane/diethyl ether gave a light orange powder (57 mg, 70%). IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3112 (w), 2964 (m), 1484 (m), 1468 (w), 1384 (w), 1369 (w), 1274 (w), 1242 (w), 1173 (w), 1152 (w), 1054 (s), 904 (w), 858 (w), 733 (w), 694 (w), 520 (w), 488 (w); $^1$H NMR (300 MHz, $CDCl_3$) δ 5.58-5.57 (m, 1H, Cp$^t$), 5.49 (m, dddd by decoupling, $J_{1\text{-}2}$ = 9.5 Hz, $J_{1\text{-}7endo}$ = 4.0 Hz, $J_{1\text{-}7exo}$ < 2 Hz, $J_{1\text{-}6exo}$ < 2 Hz, 1H, $H_1$), 5.33 (dd, $J_{2\text{-}1}$ = 9.5 Hz, $J_{2\text{-}7exo}$ = 0.8 Hz, 1H, $H_2$), 5.27-5.24 (m, 1H, Cp$^t$), 5.24-5.20 (m, 1H, Cp$^t$), 5.10 (dd, $J_{5\text{-}6endo}$ = 8.4 Hz, $J_{5\text{-}6exo}$ = 4.8 Hz, 1H, $H_5$), 4.96-4.94 (m, 1H, Cp$^t$), 2.89 (dddd, $J_{7endo\text{-}7exo}$ = 17.3 Hz, $J_{7endo\text{-}6exo}$ ≈ $J_{7endo\text{-}6exo}$ ≈ 9 Hz, $J_{7endo\text{-}1}$ = 4 Hz, 1H, $H_{7endo}$), 2.41 (s, 3H, $Me_4$), 1.93 (m, dddd by decoupling, $J_{7exo\text{-}7endo}$ = 17.1 Hz, $J_{7exo\text{-}6exo}$ = 6.3 Hz, $J_{7exo\text{-}1}$ < 2 Hz, $J_{7exo\text{-}2}$ < 2 Hz, 1H, $H_{7exo}$), 1.75-1.65 (m, 1H, $H_{6endo}$), 1.63 (s, 9H, $C_3$ *t*-Bu), 1.40 (s, 9H, Cp$^t$ *t*-Bu), 0.20 (dddd, $J_{6exo\text{-}6endo}$ = 12.7 Hz, $J_{6exo\text{-}7endo}$ = 11.5 Hz, $J_{6exo\text{-}7exo}$ = 6.5 Hz, $J_{6exo\text{-}5}$ = 7 Hz, 1H, $H_{6exo}$); $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) δ 5.57 (Cp$^t$) ↔ δ 5.24 (Cp$^t$), δ 5.20 (Cp$^t$), δ 4.94 (Cp$^t$); δ 5.49 ($H_1$) ↔ δ 5.33 ($H_2$), δ 2.89 ($H_{7endo}$), δ 1.93 ($H_{7exo}$), δ 1.65 (w, $H_{6endo}$); δ 5.33 ($H_2$) ↔ δ 2.41 (Me), δ 1.93 ($H_{7exo}$); δ 5.24 (Cp$^t$) ↔ δ 5.20 (Cp$^t$), δ 4.94 (Cp$^t$); δ 5.10 ($H_1$) ↔ δ 2.89 ($H_{7endo}$), δ 2.41 ($Me_4$), δ 1.63 ($C_3$ *t*-Bu), δ 0.20 ($H_{endo}$); δ 2.89 ($H_{7endo}$) ↔ δ 1.93 ($H_{7exo}$), δ 1.65 (w, $H_{6endo}$), δ 0.20 ($H_{endo}$); δ 1.93 ($H_{7exo}$) ↔ δ 1.65 (w, $H_{6endo}$), δ 0.20 ($H_{endo}$); δ 1.65 ($H_{6endo}$) ↔ δ 0.20 ($H_{endo}$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 136.4 (s, $C_3$), 120.1 (s, Cp$^t$ ring quaternary), 106.5 (s, $C_4$), 89.3 (dd, $^1J_{CH}$ = 167.8 Hz, $^2J_{CH}$ = 9.2 Hz, $C_2$), 86.5 (dd, $^1J_{CH}$ = 181.7 Hz, $^2J_{CH}$ = 6.1 Hz, Cp$^t$), 85.3$^a$ (d, $^1J_{CH}$ = 177.7 Hz), 85.2$^a$ (d, $^1J_{CH}$ = 179.4 Hz), 84.5 (dd, $^1J_{CH}$ = 180.3 Hz, $^2J_{CH}$ = 5.9 Hz, Cp$^t$), 84.2 (d, $^1J_{CH}$ = 157.3 Hz, $C_1$), 41.1 (t, $^1J_{CH}$ = 136.1 Hz, $C_7$), 36.8 (s, $C_3$ *t*-Bu quaternary), 32.2 (q, $^1J_{CH}$ = 127.1 Hz, $C_3$ *t*-Bu), 31.6 (s, Cp$^t$ *t*-Bu quaternary), 31.0 (q, $^1J_{CH}$ = 126.2 Hz, Cp$^t$ *t*-Bu), 25.8 (t, $^1J_{CH}$ = 132.3 Hz, $C_6$), 25.6 (q, $^1J_{CH}$ = 129.3 Hz,

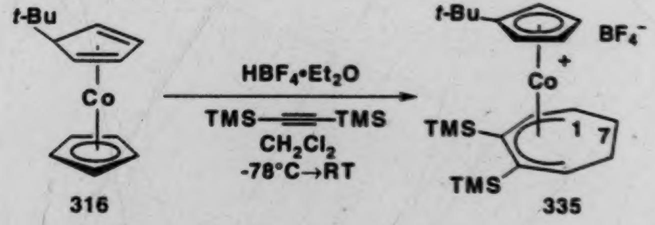
$Me_4$). [a]2 carbons overlap for one of these signals. $C_5$ and 2 C's for the Cp ring resonate at these 2 positions. HMQC (300 MHz, $CDCl_3$) δ 89.3 ($C_2$) ↔ δ 5.33 ($H_2$); δ 86.5 ($Cp^t$) ↔ δ 5.20 ($Cp^t$); δ 85[a] ($C_5$, $Cp^t$) ↔ δ 5.24 ($Cp^t$), δ 5.10 ($H_5$), δ 4.94 ($Cp^t$); δ 84.5 ($Cp^t$) ↔ δ 5.57 ($Cp^t$); δ 84.2 ($C_1$) ↔ δ 5.49 ($H_1$); δ 41.1 ($C_7$) ↔ δ 2.89 ($H_{7endo}$), δ 1.93 ($H_{7exo}$); δ 32.2 ($C_3$ *t*-Bu) ↔ δ 1.63 ($C_3$ *t*-Bu); δ 31.0 ($Cp^t$ *t*-Bu) ↔ δ 1.40 ($Cp^t$ *t*-Bu); δ 25.8 ($C_6$) ↔ δ 1.65 ($H_{6exo}$), δ 0.20 ($H_{6exo}$); δ 25.6 ($Me_4$) ↔ δ 2.41 ($Me_4$). [a]Unresolved signals in $^{13}C$ spectrum. HMBC (300 MHz, $CDCl_3$) δ 136.4 ($C_3$) ↔ δ 5.10 ($H_5$), δ 2.41 ($Me_4$), δ 1.63 ($C_3$ *t*-Bu); δ 120.1 ($Cp^t$ *t*-Bu ring quaternary) ↔ δ 5.57 ($Cp^t$), δ 5.24 ($Cp^t$), δ 5.20 ($Cp^t$), δ 4.94 ($Cp^t$), δ 1.40 ($C_3$ *t*-Bu); δ 106.5 ($C_4$) ↔ δ 5.33 ($H_2$), δ 2.41 ($Me_4$), δ 0.20 ($H_{6exo}$); δ 89.3 ($Cp^t$) ↔ δ 5.57 ($Cp^t$); δ 86.5 ($Cp^t$) ↔ δ 5.57 ($Cp^t$), δ 5.24 ($Cp^t$), δ 4.94 ($Cp^t$); δ 85[a] ↔ δ 5.57 ($Cp^t$), δ 5.24 ($Cp^t$), δ 5.20 ($Cp^t$), δ 4.94 ($Cp^t$), δ 2.41 ($Me_4$), δ 0.20 ($H_{6exo}$); δ 84[b] ↔ δ 5.24 ($Cp^t$), δ 5.20 ($Cp^t$), δ 4.94 ($Cp^t$), δ 2.89 ($H_{7endo}$); δ 41.1 ($C_7$) ↔ δ 5.33 ($H_2$), δ 5.10 ($H_5$), δ 0.20 ($H_{6exo}$); δ 36.8 ($C_3$ *t*-Bu quaternary) ↔ δ 5.33 ($H_2$), δ 1.63 ($C_3$ *t*-Bu); δ 31.0 ($Cp^t$ *t*-Bu quaternary) ↔ δ 1.40 ($C_3$ *t*-Bu); δ 25[c] ↔ δ 5.10 ($H_5$), δ 2.89 ($H_{7endo}$). [a]Signals at 85.3 and 85.2 ($C_5$ and $Cp^t$) overlap. [b]Signals at 84.5 ($Cp^t$) and 84.2 ($C_1$) overlap. [c]Signals at 25.8 ($C_6$) and 25.6 ($C_{10}$) overlap. Analysis calculated for $C_{21}H_{32}BCoF_4$: C, 58.63; H, 7.51; found: C, 58.484; H, 7.729.



316 334

**[(*t*-Bu$C_5H_4$)Co(3-($Me_3Si$)-4-Me-$\eta^5$-$C_7H_7$]$^+$ $BF_4^-$ (334).** In the drybox, ($C_5H_5$)Co($\eta^4$-1-*t*-Bu-$C_5H_5$) (**316**) (34.7 mg, 0.141 mmol) was weighed into a Schlenk flask. The compound was dissolved in degassed dichloromethane (5 mL) and cooled to -78 °C. To the solution was added 1-trimethylsilylpropyne (0.15 mL, 7 equiv), followed by $HBF_4$•$Et_2O$ (0.46 μL, 2.2 equiv). The color of the red solution deepened immediately upon addition of the acid. The solution was slowly warmed with stirring over a 12 h period. The solvent was removed and the crude residue was redissolved in dichloromethane (3 mL) and filtered through a Celite column. Addition of diethyl ether (50 mL) caused an orange precipitate (45.6 mg, 72%) to form. Recrystallization from dichloromethane/diethyl ether gave orange-red crystals (29.6 mg, 47%). IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3113 (w), 2962 (m), 1486 (m), 1468 (m), 1434 (m), 1384 (m), 1266 (m), 1151 (m), 1053 (s), 978 (m), 912 (m), 838 (s), 761 (m), 724 (w), 697 (w), 622 (w), 520 (m); $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.67 (br d, dddd by decoupling, $J_{1\text{-}2}$ = 9.3 Hz, $J_{1\text{-}7\text{exo}}$ = $J_{1\text{-}7\text{exo}}$ = 3.5 Hz, $J_{1\text{-}6\text{endo}}$ <2 Hz, 1H, $H_1$), 5.55-5.40 (m, 2H, $Cp^t$), 5.46-5.43 (m, 1H, $Cp^t$), 5.22 (d, $J_{2\text{-}1}$ = 9 Hz, 1H, $H_2$), 5.19 (dd, $J_{5\text{-}6\text{endo}}$ = 8.2 Hz, $J_{5\text{-}6\text{exo}}$ = 5.0 Hz, 1H, $H_5$), 5.03-5.00 (m, 1H, $Cp^t$), 2.99 (m, dddd by decoupling, $J_{7\text{endo-}7\text{exo}}$ = 17.6 Hz, $J_{7\text{endo-}6\text{exo}}$ = 11.7 Hz, $J_{7\text{endo-}6\text{endo}}$ = 9.7 Hz, $J_{7\text{endo-}1}$ = 3.5 Hz, 1H, $H_{7\text{endo}}$), 2.60 (s, 3H, $Me_4$), 2.01 (br d, dddd by decoupling, $J_{7\text{exo-}7\text{endo}}$ = 17.6 Hz, $J_{7\text{exo-}6\text{exo}}$ = 5.8 Hz, $J_{7\text{exo-}1}$ = 3.5 Hz, $J_{7\text{exo-}6\text{endo}}$ < 2 Hz, 1H, $H_{7\text{exo}}$), 1.80 (m, ddddd by decoupling, $J_{6\text{endo-}6\text{exo}}$ = 11.7 Hz, $J_{6\text{endo-}7\text{endo}}$ = 9.7 Hz, $J_{6\text{endo-}5}$ = 8.2 Hz, $J_{6\text{endo-}7\text{exo}}$ < 2 Hz, $J_{6\text{endo-}1}$ = 2Hz, 1H, $H_{6\text{endo}}$), 1.30 (s, 9H, $Cp^t$ *t*-Bu), 0.41 (s, 9H, $SiMe_3$), 0.23 (dddd, $J_{6\text{exo-}6\text{endo}}$ = $J_{6\text{exo-}7\text{endo}}$ = 11.7 Hz, $J_{6\text{exo-}7\text{exo}}$ = 5.8 Hz, $J_{6\text{exo-}5}$ = 5.0 Hz, 1H, $H_{6\text{exo}}$); $^1H$-$^1H$ GCOSY (300 MHz, $CDCl_3$) δ 5.67 ($H_1$) ↔ δ 5.22 ($H_2$), δ 2.99 ($H_{7\text{endo}}$), δ 2.01 ($H_{7\text{exo}}$), δ 1.80 (w, $H_{6\text{endo}}$); δ 5.47 ($Cp^t$) ↔ δ 5.02 ($Cp^t$); δ 5.45 ($Cp^t$) ↔ δ 5.02 ($Cp^t$); δ 5.22 ($H_2$) ↔ δ 2.60 (w, $Me_4$), δ 2.01 ($H_{7\text{exo}}$); δ 5.19 ($H_5$) ↔ δ 1.80 ($H_{6\text{endo}}$), δ 0.23 ($H_{6\text{exo}}$); δ 2.99 ($H_{7\text{endo}}$) ↔ δ 2.01 ($H_{7\text{exo}}$), δ 1.80 ($H_{6\text{endo}}$), δ 0.23 ($H_{6\text{exo}}$); δ 2.01 ($H_{7\text{exo}}$) ↔ δ 0.23 ($H_{6\text{exo}}$); δ 1.80 ($H_{6\text{endo}}$) ↔ δ 0.23 ($H_{6\text{exo}}$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 122.3 (s, $C_3$), 119.6 (s, $Cp^t$ ring quaternary), 102.2 (s, $C_4$), 94.6 (d, $^1J_{CH}$ = 164.9 Hz, $C_2$), 89.2 (d, $^1J_{CH}$ = 155.4 Hz, $C_1$), 87.7 (d, $^1J_{CH}$ = 155.5 Hz, $C_5$), 85.7 (d, $^1J_{CH}$ = 183.5 Hz, $Cp^t$), 85.2 (d, $^1J_{CH}$ = 180.2 Hz, $Cp^t$), 84.3 (d, $^1J_{CH}$ = 182.5 Hz, $Cp^t$), 83.8 (d, $^1J_{CH}$ = 178.9 Hz, $Cp^t$), 41.9 (t, $^1J_{CH}$ = 130.8 Hz, $C_7$), 31.6 (s, *t*-Bu quaternary), 30.9 (q, $^1J_{CH}$ = 126.9 Hz, *t*-Bu), 27.3 (t, $^1J_{CH}$ = 131.1 Hz, $C_6$), 23.3 (q, $^1J_{CH}$ = 132.7 Hz, $Me_4$), 0.05 (q, $^1J_{CH}$ = 120.1 Hz, $SiMe_3$);

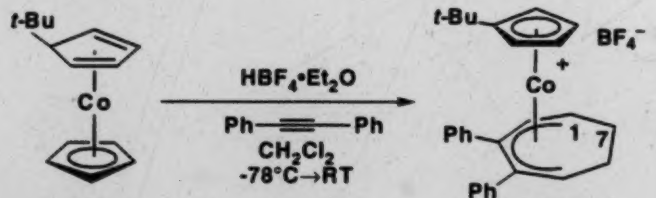
HMQC (300 MHz, CDCl$_3$) δ 94.6 (C$_2$) ↔ δ 5.22 (H$_2$); δ 89.2 (C$_1$) ↔ δ 5.67 (H$_1$); δ 87.7 (C$_5$) ↔ δ 5.19 (H$_5$); δ 85.7 (Cp$^t$) ↔ δ 5.52 (Cp$^t$); δ 85.2 (Cp$^t$) ↔ δ 5.44 (Cp$^t$); δ 84.3 (Cp$^t$) ↔ δ 5.02 (Cp$^t$); δ 83.8 (Cp$^t$) ↔ δ 5.50 (Cp$^t$); δ 41.9 (C$_7$) ↔ δ 2.99 (H$_{7endo}$), δ 2.01 (H$_{7exo}$); δ 30.9 (*t*-Bu) ↔ δ 1.30 (*t*-Bu); δ 27.3 (C$_6$) ↔ δ 1.80 (H$_{6endo}$), δ 0.23 (H$_{6exo}$); δ 23.3 (Me$_4$) ↔ δ 2.60 (Me$_4$); δ 0.05 (SiMe$_3$) ↔ δ 0.41 (SiMe$_3$); HMBC (300 MHz, CDCl$_3$) δ 122.3 (C$_3$) ↔ δ 5.22 (H$_2$), δ 5.19 (H$_5$), δ 2.60 (Me$_4$); δ 119.6 (Cp$^t$ ring quaternary) ↔ δ 5.50 (Cp$^t$), δ 5.40 (Cp$^t$), δ 1.30 (*t*-Bu); δ 102.2 (C$_4$) ↔ δ 5.22 (H$_2$), δ 2.60 (Me$_4$), δ 1.80 (H$_{6endo}$), δ 0.23 (H$_{6exo}$); δ 94.6 (C$_2$) ↔ δ 2.60 (Me$_4$); δ 89.2 (C$_1$) ↔ δ 1.80 (H$_{6endo}$); δ 87.7 (C$_5$) ↔ δ 1.80 (H$_{6endo}$), δ 0.23 (H$_{6exo}$); δ $^a$85.7, δ 85.2$^a$, δ 84.3$^a$, δ 83.8$^a$ ↔ δ 5.50 (Cp$^t$), δ 5.43 (Cp$^t$), δ 5.00 (Cp$^t$); δ 41.9 (C$_7$) ↔ δ 5.22 (H$_2$), δ 5.19 (H$_5$), δ 2.60 (Me$_4$), δ 1.80 (H$_{6endo}$), δ 0.23 (H$_{6exo}$); δ 30.9 (*t*-Bu) ↔ δ 1.30 (*t*-Bu); δ 27.3 (C$_6$) ↔ δ 5.19 (H$_5$); δ 23.3 (Me$_4$) ↔ δ 5.22 (H$_2$); δ 0.05 (SiMe$_3$) ↔ δ 0.41 (SiMe$_3$). $^a$Resolution of these signals is poor. Analysis calculated for C$_{20}$H$_{32}$BCoF$_4$Si: C, 53.82; H, 7.23; found: C, 53.434; H, 6.884.



**[(η$^5$-1-*t*-Bu-C$_5$H$_4$)Co(η$^5$-3,4-(Me$_3$Si)$_2$-C$_7$H$_7$]$^+$ BF$_4^-$ (335).** In the drybox, CpCo(η$^4$-1-*t*-Bu-C$_5$H$_5$) (**316**) (102.9 mg, 0.4179 mmol) was weighed into a Schlenk flask. The compound was dissolved in degassed dichloromethane (20 mL) and cooled to -78 °C. To the solution was added bis(trimethylsilyl)acetylene (0.47 mL, 5 equiv), followed by HBF$_4$•Et$_2$O (0.135 mL, 2.2 equiv). The color of the red solution deepened immediately upon addition of the acid. The solution was slowly warmed with stirring over a 12 h period. The solvent was removed and the crude residue was redissolved in dichloromethane (5 mL) and filtered through a Celite column. Addition of diethyl ether

(100 mL) caused an orange precipitate (165.9 mg, 79%) to form. Recrystallization from dichloromethane/diethyl ether gave orange-red crystals (156.4 mg, 74%). Crystals suitable for X-ray crystallographic analysis were grown by layering diethyl ether on top of a dichloromethane solution. For full data on this crystal structure, request report # JMS9716 from the Structure Determination Laboratory at the University of Alberta Department of Chemistry. IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3116 (w), 2961 (m), 1486 (m), 1457 (m), 1393 (m), 1365 (w), 1254 (s), 1151 (m), 1055 (s), 979 (m), 906 (m), 866 (s), 834 (s), 760 (m), 698 (w), 638 (w), 520 (m); $^1$H NMR (400 MHz, $CDCl_3$) δ 5.94 (br d, $J_{obs}$ = 9 Hz, dddd by decoupling, $J_{1\text{-}2}$ = 9.2 Hz, $J_{1\text{-}7endo}$ = $J_{1\text{-}7exo}$ = 3.3 Hz, $J_{1\text{-}6endo}$ < 2 Hz, 1H, $H_1$), 5.84-5.85 (narrow m, 1H, $Cp^t$), 5.33 (dd, $J_{5\text{-}6endo}$ = 8.2 Hz, $J_{5\text{-}6exo}$ = 5.2 Hz, 1H, $H_5$), 5.28 (d, $J_{2\text{-}1}$ = 9.2 Hz, 1H, $H_2$), 5.20-5.22 (narrow m, 1H, $Cp^t$), 5.07-5.09 (narrow m, 1H, $Cp^t$), 4.92-4.94 (narrow m, 1H, $Cp^t$), 3.05 (m, dddd by decoupling, $J_{7endo\text{-}7exo}$ = 17.7 Hz, $J_{7endo\text{-}6endo}$ = $J_{7endo\text{-}6exo}$ = 9.5 Hz, $J_{7endo\text{-}1}$ = 3.7 Hz, 1H, $H_{7endo}$), 2.08 (br dd, $J_{obs}$ = 17.3, 5.4 Hz, dddd by decoupling, $J_{7exo\text{-}7endo}$ = 17.7 Hz, $J_{7exo\text{-}6exo}$ = 6.0 Hz, $J_{7exo\text{-}1}$ = 2.7 Hz, $J_{7exo\text{-}2}$ < 1Hz, 1H, $H_{7exo}$), 1.72 (br q, $J_{obs}$ = 11 Hz, ddd by decoupling, $J_{6endo\text{-}6exo}$ = 12.3 Hz, $J_{6endo\text{-}7endo}$ = $J_{6endo\text{-}5}$ = 8.5 Hz, $J_{6endo\text{-}1}$ < 2 Hz, 1H, $H_{6endo}$), 1.42 (s, 9H, *t*-Bu), 0.55 (s, 9H, $C_3$ $SiMe_3$), 0.41 (s, 9H, $C_4$ $SiMe_3$), 0.15 (apparent tt, $J_{6exo\text{-}6endo}$ = 12.3 Hz, $J_{6exo\text{-}7endo}$ = 9.5 Hz, $J_{6exo\text{-}7exo}$ = 6.0 Hz, $J_{6exo\text{-}5}$ = 5.2 Hz, 1H, $H_{6exo}$); $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) δ 5.94 ($H_1$) ↔ δ 5.28 ($H_2$), δ 3.05 ($H_{7endo}$), δ 2.08 ($H_{7exo}$), δ 1.72 ($H_{6endo}$); δ 5.84 ($Cp^t$) ↔ δ 5.20 ($Cp^t$), δ 5.07 ($Cp^t$), δ 4.92 ($Cp^t$); δ 5.33 ($H_5$) ↔ δ 1.72 ($H_{6endo}$), δ 0.15 ($H_{6exo}$); δ 5.28 ($H_2$) ↔ δ 2.08 ($H_{7exo}$); δ 5.20 ($Cp^t$) ↔ δ 5.07 ($Cp^t$), δ 4.92 ($Cp^t$); δ 5.07 ($Cp^t$) ↔ δ 4.92 ($Cp^t$); δ 3.05 ($H_{7endo}$) ↔ δ 2.08 ($H_{7exo}$), δ 1.72 ($H_{6endo}$), δ 0.15 ($H_{6exo}$); δ 2.08 ($H_{7exo}$) ↔ δ 0.15 ($H_{6exo}$); δ 1.72 ($H_{6endo}$) ↔ δ 0.15 ($H_{6exo}$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 121.6 (s, $C_3$), 120.0 (s, $Cp^t$ ring quaternary), 107.7 (s, $C_4$), 98.1 (dd, $^1J_{CH}$ = 166.0 Hz, $^2J_{CH}$ = 8.9 Hz, $C_2$), 91.6 (d, $^1J_{CH}$ = 156.3 Hz, $C_1$), 88.9 (d, $^1J_{CH}$ = 156.2 Hz, $C_5$), 86.8 (d, $^1J_{CH}$ = 182.0 Hz, $Cp^t$), 84.5 (d, $^1J_{CH}$ = 181.1 Hz, $Cp^t$), 83.0 (d, $^1J_{CH}$ = 183.9 Hz, $Cp^t$), 82.7 (d, $^1J_{CH}$ = 178.1 Hz, $Cp^t$), 42.5 (t, $^1J_{CH}$ =

130.2 Hz, $C_7$), 31.8 (s, *t*-Bu quaternary), 31.2 (q, $^1J_{CH}$ = 126.9 Hz, *t*-Bu), 27.1 (t, $^1J_{CH}$ = 131.5 Hz, $C_6$), 2.07 (q, $^1J_{CH}$ = 120.7 Hz, $C_3$ $SiMe_3$), 1.63 (q, $^1J_{CH}$ = 119.9 Hz, $C_4$ $SiMe_3$); HMQC (300 MHz, $CDCl_3$) δ 98.1 ($C_2$) ↔ δ 5.28 ($H_2$); δ 91.6 ($C_1$) ↔ δ 5.94 ($H_1$); δ 88.9 ($C_5$) ↔ δ 5.33 ($H_5$); δ 86.8 ($Cp^t$) ↔ δ 5.84 ($Cp^t$); δ 84.5 ($Cp^t$) ↔ δ 5.07 ($Cp^t$); δ 83.0 ($Cp^t$) ↔ δ 4.92 ($Cp^t$); δ 82.7 ($Cp^t$) ↔ δ 5.20 ($Cp^t$); δ 42.5 ($C_7$) ↔ δ 3.05 ($H_{7endo}$), δ 2.08 ($H_{7exo}$); δ 31.2 (*t*-Bu) ↔ δ 1.42 (*t*-Bu); δ 27.1 ($C_6$) ↔ δ 1.72 ($H_{6endo}$), δ 0.15 ($H_{6exo}$); δ 2.07 ($C_3$ $SiMe_3$) ↔ δ 0.55 ($C_3$ $SiMe_3$); δ 1.63 ($C_4$ $SiMe_3$) ↔ δ 0.41 ($C_4$ $SiMe_3$); HMBC (300 MHz, $CDCl_3$) δ 121.6 ($C_3$) ↔ δ 5.33 ($H_5$), δ 5.28 ($H_2$); δ 120.0 ($Cp^t$ ring quaternary) ↔ δ 5.20 ($Cp^t$), δ 5.07 ($Cp^t$), δ 4.94 ($Cp^t$), δ 1.42 (*t*-Bu); δ 107.7 ($C_4$) ↔ δ 5.33 ($H_5$), δ 5.28 ($H_2$), δ 1.72 ($H_{6endo}$), δ 0.15 ($H_{6exo}$); δ 98.1 ($C_2$) ↔ δ 3.05 ($H_{7endo}$); δ 91.6 ($C_1$) ↔ δ 3.05 ($H_{7endo}$), δ 1.72 ($H_{6endo}$); δ 88.9 ($C_5$) ↔ δ 2.08 ($H_{7exo}$), δ 1.72 ($H_{6endo}$), δ 0.15 ($H_{6exo}$); δ 86.8[a], δ 84.5[a], δ 83.0[a], δ 82.7[a] ($Cp^t$) ↔ δ 5.84 ($Cp^t$), δ 5.20 ($Cp^t$), δ 5.07 ($Cp^t$), δ 4.92 ($Cp^t$); δ 42.5 ($C_7$) ↔ δ 5.33 ($H_5$), δ 5.28 ($H_2$), δ 1.72 ($H_{6endo}$), δ 0.15 ($H_{6exo}$); δ 31.8/31.2 (*t*-Bu and *t*-Bu quaternary) ↔ δ 1.42 (*t*-Bu); δ 27.1 ($C_6$) ↔ δ 5.33 ($H_5$), δ 3.05 ($H_{7endo}$); δ 2.07 ($C_3$ $SiMe_3$) ↔ δ 0.55 ($C_3$ $SiMe_3$); δ 1.63 ($C_4$ $SiMe_3$) ↔ δ 0.41 ($C_4$ $SiMe_3$). [a]Signals overlap. Analysis calculated for $C_{22}H_{38}BCoF_4Si_2$: C, 52.38; H, 7.59; found: C, 52.075; H, 7.586.



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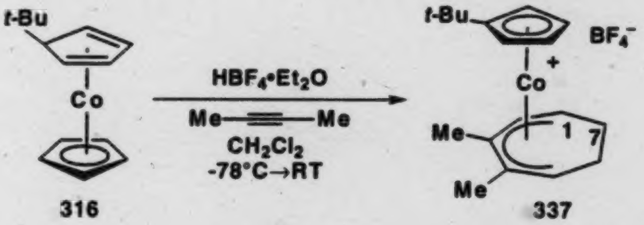
**[($C_5H_4t$-Bu)Co($\eta^5$-3,4-$Ph_2$-$C_7H_7$)]$^+$ $BF_4^-$ (336).** A solution of CpCo($\eta^4$-1-*t*-Bu-$C_5H_5$) (**316**) (42.1 mg, 0.171 mmol) in dichloromethane (5 mL) was prepared under nitrogen and cooled to -78 °C. To the solution was added diphenylacetylene (0.305 g, 10 equiv), followed by $HBF_4$•$Et_2O$ (55 μL, 2.2 equiv). The solution darkened immediately upon addition of the acid. The solution was slowly warmed with stirring over a 12 h period.

Removal of the solvent was followed by flash chromatography on silica gel using 5% methanol/dichloromethane. Recrystallization from dichloromethane/diethyl ether gave 61 mg (70%) of a light orange powder. IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3110 (w), 3059 (w), 3033 (w), 2965 (w), 2909 (w), 2876 (w), 1485 (w), 1464 (w), 1449 (w), 1420 (w), 1398 (w), 1370 (w), 1273 (w), 1150 (w), 1056 (s), 1036 (s), 1003 (m), 914 (m), 859 (w), 837 (w), 766 (m), 728 (m), 702 (s), 681 (w), 647 (w); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, $J$ = 6.5 Hz, 2H, $H_{Ph}$), 7.4-7.4 (m, 2H, $H_{Ph}$), 7.3-7.15 (m, 6H, $H_{Ph}$), 6.09 (br s, 1H, $Cp^t$), 5.9-5.8 (m, 2H, $H_{1,2}$), 5.59 (dd, $J_{5\text{-}6exo}$ = 8.4 Hz, $J_{5\text{-}6endo}$ = 4.7 Hz, 1H, $H_5$), 5.41 (br s, 1H, $Cp^t$), 5.12 (br s, 1H, $Cp^t$), 4.29 (br s, 1H, $Cp^t$), 3.21-3.10 (m, 1H, $H_{7endo}$), 2.18-2.06 (m, 2H, $H_{7exo,\ 6endo}$), 1.30 (s, 9H, *t*-Bu), 0.74-0.65 (m, 1H, $H_{6exo}$); $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) δ 7.54 ($H_{Ph}$) ↔ δ 7.45 ($H_{Ph}$); δ 6.09 ($Cp^t$) ↔ δ 5.41 ($Cp^t$), δ 5.12 ($Cp^t$), δ 4.29 ($Cp^t$); δ 5.9 ($H_{1,2}$) ↔ δ 5.8 ($H_{1,2}$), δ 3.15 ($H_{7endo}$), δ 2.12 ($H_{7exo,6endo}$); δ 5.59 ($H_5$) ↔ δ 2.12 ($H_{7exo,6endo}$), δ 2.04 ($H_{7exo,6endo}$), δ 0.70 ($H_{6exo}$); δ 5.41 ($Cp^t$) ↔ δ 5.12 ($Cp^t$), δ 4.29 ($Cp^t$); δ 5.12 ($Cp^t$) ↔ δ 4.29 ($Cp^t$); δ 3.15 ($H_{7endo}$) ↔ δ 2.1 ($H_{7exo,\ 6endo}$), δ 0.70 ($H_{6exo}$); δ 2.1 ($H_{7exo,6endo}$) ↔ δ 0.70 ($H_{6exo}$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 136.3 (s, $C_{Ph,\ ipso}$), 136.0 (s, $C_{Ph,\ ipso}$), 131.3 (dt, $^1J_{CH}$ = 159.6 Hz, $^2J_{CH}$ = 6.1 Hz, $C_{Ph}$), 130.1 (d, $^1J_{CH}$ = 160.9 Hz, $C_{Ph}$), 129.7 (d, $^1J_{CH}$ = 162.1 Hz, $C_{Ph}$), 129.3 (dd, $^1J_{CH}$ = 163.1 Hz, $^2J_{CH}$ = 7.0 Hz, $C_{Ph}$), 131.3 (dd, $^1J_{CH}$ = 162.6 Hz, $^2J_{CH}$ = 7.0 Hz, $C_{Ph}$), 122.5 (s, $Cp^t$ ring quaternary), 119.4 (s, $C_3$), 110.2 (s, $C_4$), 94.4 (d, $^1J_{CH}$ = 169.7 Hz, $C_2$), 88.9$^a$ (d, $^1J_{CH}$ = 151.1 Hz, $C_1$), 88.6$^a$ (d, $^1J_{CH}$ = 187.3 Hz, $Cp^t$), 86.2 (d, $^1J_{CH}$ = 184.6 Hz, $Cp^t$), 83.2 (d, $^1J_{CH}$ = 182.2 Hz, $Cp^t$), 81.8 (d, $^1J_{CH}$ = 153.2 Hz, $C_5$), 42.2 (t, $^1J_{CH}$ = 128.6 Hz, $C_7$), 31.8 (s, *t*-Bu quaternary), 31.0 (q, $^1J_{CH}$ = 127.6 Hz, *t*-Bu), 26.9 (t, $^1J_{CH}$ = 130.2 Hz, $C_6$). $^a$Signals overlap, $^1J_{CH}$'s are approximate. Most signals from 94.4-81.8 show small unresolved $^{2,3}J_{CH}$ coupling constants. HMQC (300 MHz, $CDCl_3$) δ 131.3 ($C_{Ph}$) ↔ δ 7.2 ($H_{Ph}$); δ 130.1 ($C_{Ph}$) ↔ δ 7.54 ($H_{Ph}$); δ 129.7 ($C_{Ph}$) ↔ δ 7.35 ($H_{Ph}$); δ 129.3 ($C_{Ph}$) ↔ δ 7.35 ($H_{Ph}$); δ 128.2 ($C_{Ph}$) ↔ δ 7.2 ($H_{Ph}$); δ 94.4 ($C_2$) ↔ δ 5.80 ($H_2$); δ 88.9 ($C_1$) ↔ δ 5.84 ($H_1$); δ 88.6 ($Cp^t$) ↔ δ 5.12 ($Cp^t$); δ 88.2 ($Cp^t$) ↔ δ 4.29

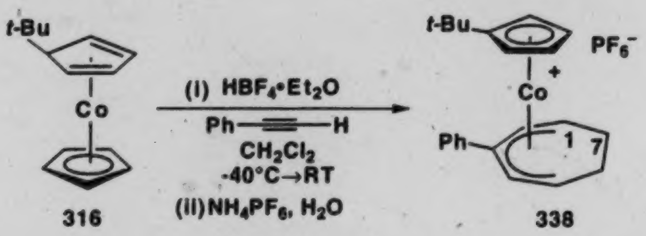
($Cp^t$); δ 86.2 ($Cp^t$) ↔ δ 5.41 ($Cp^t$); δ 83.2 ($Cp^t$) ↔ δ 6.09 ($Cp^t$); δ 81.8 ($C_5$) ↔ δ 5.59 ($H_5$); δ 42.2 ($C_7$) ↔ δ 3.15 ($H_{7endo}$), δ 2.13 ($H_{7exo}$); δ 31.0 (*t*-Bu) ↔ δ 1.30 (*t*-Bu); δ 26.9 ($C_6$) ↔ δ 2.13 ($H_{6endo}$), δ 0.70 ($H_{6exo}$); HMBC (300 MHz, $CDCl_3$) δ 136.3 ($C_{Ph,ipso}$) ↔ δ 7.17 ($H_{Ph}$), δ 5.59 ($H_5$); δ 136.0 ($C_{Ph,\ ipso}$) ↔ δ 7.35 ($H_{Ph}$), δ 5.8 ($H_{1,2}$); δ 131.3 ($C_{Ph}$) ↔ δ 7.31 ($H_{Ph}$), δ 7.24 ($H_{Ph}$); δ 130.1 ($C_{Ph}$) ↔ δ 7.24 ($H_{Ph}$); δ 129.7 ($C_{Ph}$) ↔ δ 7.54 ($H_{Ph}$); δ 129.3 ($C_{Ph}$) ↔ δ 7.37 ($H_{Ph}$), δ 7.33 ($H_{Ph}$); δ 128.2 ($C_{Ph}$) ↔ δ 7.17 ($H_{Ph}$); δ 122.5 ($Cp^t$) ↔ δ 6.09 ($Cp^t$), δ 5.41 ($Cp^t$), δ 5.12 ($Cp^t$), δ 4.29 ($Cp^t$), δ 1.30 (*t*-Bu); δ 119.4 ($C_3$) ↔ δ 7.54 ($H_{Ph}$), δ 5.80 ($H_{1,2}$), δ 5.59 ($H_5$); δ 110.2 ($C_4$) ↔ δ 7.25 ($H_{Ph}$), δ 5.80 ($H_{1,2}$), δ 2.09 ($H_{7exo,6endo}$), δ 2.05 ($H_{7exo,6endo}$), δ 0.74 ($H_{6exo}$); δ 94.4 ($C_2$) ↔ δ 6.09 ($Cp^t$), δ 3.15 ($H_{7endo}$); δ 88.9/ 88.6/ 88.2 ($Cp^t$) ↔ δ 6.09 ($Cp^t$), δ 5.41 ($Cp^t$), δ 5.12 ($Cp^t$), δ 4.29 ($Cp^t$), δ 1.30 (*t*-Bu), δ 3.15 ($H_{7endo}$), δ 2.10 ($H_{7exo}$); δ 86.2 ($Cp^t$) ↔ δ 6.09 ($Cp^t$), δ 5.12 (w, $Cp^t$), δ 4.29 ($Cp^t$); δ 83.2 ($Cp^t$) ↔ δ 5.41 ($Cp^t$), δ 5.12 ($Cp^t$), δ 4.29 ($Cp^t$); δ 81.8 ($C_5$) ↔ δ 2.10 ($H_{7exo,6endo}$), δ 2.06 ($H_{7exo,6endo}$), δ 0.74 ($H_{6exo}$); δ 42.2 ($C_7$) ↔ δ 5.9 ($H_{1,2}$), δ 5.59 ($H_5$), δ 2.15 ($H_{7exo,6endo}$), δ 0.74 ($H_{6exo}$); δ 31.8, 31.0 (*t*-Bu and *t*-Bu quaternary) ↔ δ 1.30 (*t*-Bu); δ 26.9 ($C_6$) ↔ δ 5.59 ($H_5$), δ 3.15 (w, $H_{7endo}$), δ 2.15 ($H_{7exo,6endo}$). Analysis calculated for $C_{28}H_{30}BCoF_4$: C, 65.64; H, 5.91; found: C, 65.240; H, 5.854.



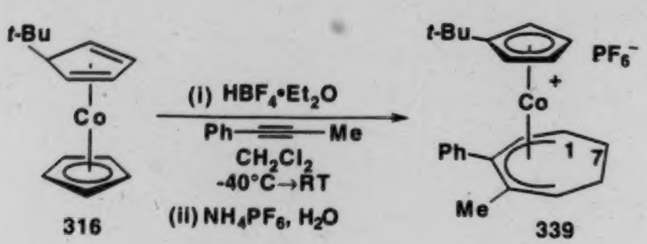
**$[(\eta^5\text{-1-}t\text{-Bu-C}_5\text{H}_4)\text{Co}(\eta^5\text{-3,4-Me}_2\text{-C}_7\text{H}_7)]^+\ \text{BF}_4^-$ (337).** In the drybox, $CpCo(\eta^4\text{-1-}t\text{-Bu-}C_5H_5)$ (**316**) (0.2059 g, 0.8362 mmol) was weighed into a Schlenk flask. The compound was dissolved in degassed dichloromethane (20 mL) and cooled to -40 °C. To the solution was added $HBF_4$•$Et_2O$ (0.135 mL, 1.1 equiv). The color of the red solution turned a deep green upon addition of the acid. After stirring 1 min at -40°C, 2-butyne

(0.196 mL, 3 equiv) was added, changing the color of the solution to a dark red. The solution was slowly warmed with stirring to room temperature. A drop of saturated aqueous $NaHCO_3$ was added and all volatile material was removed *in vacuo*. The crude residue was redissolved in dichloromethane and filtered through a Celite column. Addition of diethyl ether caused an orange-brown precipitate (0.2416 g, 74%) to form. IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3112 (m), 2965 (s), 2875 (m), 1695 (w), 1485 (s), 1463 (m), 1372 (m), 1278 (m), 1152 (m), 1054 (s), 867 (m), 520 (m), 495 (w); $^1$H NMR (360 MHz, $CDCl_3$) δ 5.59-5.55 (m, 1H, Cp$^t$), 5.41-5.38 (m, Cp$^t$), 5.36-5.32 (m, 2H, $H_{1,2}$), 5.25 (dd, $J_{5\text{-}6endo}$ = 8.1 Hz, $J_{5\text{-}6exo}$ = 4.4 Hz, 1H, $H_5$), 5.24-5.22 (m, 1H, Cp$^t$), 5.10-5.07 (m, 1H, Cp$^t$), 2.77 (dddd, $J_{7endo\text{-}7exo}$ = 17.2 Hz, $J_{7endo\text{-}6endo}$ = $J_{7endo\text{-}6exo}$ = 9.6 Hz, $J_{7endo\text{-}1}$ = 4.1 Hz, 1H, $H_{7endo}$), 2.58 (s, 3H, $Me_3$), 2.31 (s, 3H, $Me_4$), 2.00-1.88 (m, $J_{6endo\text{-}6exo}$ = 13.8 Hz, $J_{6endo\text{-}7endo}$ = 9.6 Hz, $J_{6endo\text{-}5}$ = 8.1 Hz, $J_{6endo\text{-}7exo}$ = 1.9 Hz, 1H, $H_{6endo}$), 1.76 (m, dddd by decoupling, $J_{7exo\text{-}7endo}$ = 16.9 Hz, $J_{7exo\text{-}6exo}$ = 6.1 Hz, $J_{7exo\text{-}1}$ = small, $J_{7exo\text{-}6endo}$ = 1.9 Hz, 1H, $H_{7exo}$), 1.30 (s, 9H, *t*-Bu), 0.45 (dddd, $J_{6exo\text{-}6endo}$ = 13.8 Hz, $J_{6exo\text{-}7endo}$ = 10.2 Hz, $J_{6exo\text{-}7exo}$ = 6.3 Hz, $J_{6exo\text{-}5}$ = 4.5 Hz, 1H, $H_{6exo}$); $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) δ 5.59 (Cp$^t$) ↔ δ 5.39 (Cp$^t$), δ 5.23 (Cp$^t$), δ 5.08 (Cp$^t$); δ 5.39 (Cp$^t$) ↔ δ 5.23 (Cp$^t$), δ 5.08 (Cp$^t$); δ 5.34 ($H_{1,2}$) ↔ δ 2.77 ($H_{7endo}$), δ 1.75 ($H_{7exo}$); δ 5.25 ($H_5$) ↔ δ 1.93 ($H_{6endo}$), δ 0.45 ($H_{6exo}$); δ 5.23 (Cp$^t$) ↔ δ 5.08 (Cp$^t$); δ 2.77 ($H_{7endo}$) ↔ δ 1.93 ($H_{6endo}$), δ 1.75 ($H_{7exo}$), δ 0.45 ($H_{6exo}$); δ 1.93 ($H_{6endo}$) ↔ δ 1.75 ($H_{7exo}$), δ 0.45 ($H_{6exo}$); δ 1.75 ($H_{7exo}$) ↔ δ 0.45 ($H_{6exo}$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 120.2 (s, $C_3$), 117.3 (s, Cp$^t$), 109.1 (s, $C_4$ ), 93.7 (d, $^1J_{CH}$ = 170.4 Hz, $C_2$), 87.0$^a$ (d, $^1J_{CH}$ = 183.3 Hz, Cp$^t$), 86.9$^a$ (d, $^1J_{CH}$ = 183.3 Hz, Cp$^t$), 85.9 (d, $^1J_{CH}$ = 158.0 Hz, $C_1$), 85.5 (d, $^1J_{CH}$ = 165 Hz, $C_5$), 84.56$^b$ (d, $^1J_{CH}$ = 181.7 Hz, Cp$^t$), 84.53$^b$ (d, $^1J_{CH}$ = 183.3 Hz, Cp$^t$), 39.7 (t, $^1J_{CH}$ = 131.8 Hz, $C_7$), 31.5 (s, *t*-Bu quaternary), 30.9 (q, $^1J_{CH}$ = 127.3 Hz, *t*-Bu), 27.7 (t, $^1J_{CH}$ = 125.2 Hz, $C_6$), 23.0 (q, $^1J_{CH}$ ≈ 125 Hz, $Me_4$), 21.5 (q, $^1J_{CH}$ = 126.9 Hz, $Me_3$). $^{a,b}$ Carbon signals overlap in gated spectrum. HMQC (300 MHz, $CDCl_3$) δ 93.7 ($C_2$) ↔ δ 5.34 ($H_{1,2}$); δ 87.0 (Cp$^t$) ↔ δ 5.08 (Cp$^t$); δ 86.9 (Cp$^t$) ↔ δ 5.57 (Cp$^t$); δ 85.9 ($C_1$) ↔ δ

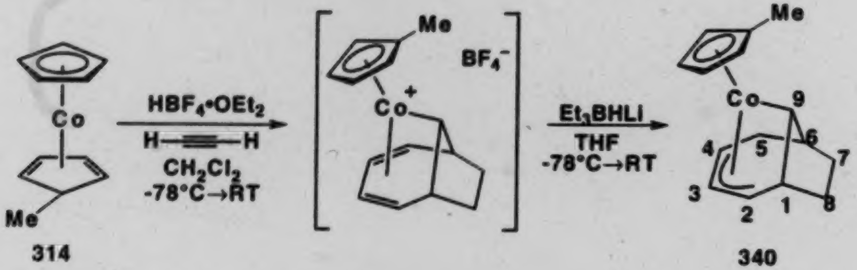
5.34 ($H_{1,2}$); δ 85.5 ($C_5$) ↔ δ 5.25 ($H_5$); δ 84.6[a] ($Cp^t$) ↔ δ 5.39 ($Cp^t$); δ 84.6[a] ($Cp^t$) ↔ δ 5.23 ($Cp^t$); δ 39.7 ($C_7$) ↔ δ 2.77 ($H_{7endo}$), δ 1.75 ($H_{7exo}$); δ 30.9 (*t*-Bu) ↔ δ 1.30 (*t*-Bu); δ 27.7 ($C_6$) ↔ δ 1.93 ($H_{6endo}$), δ 0.45 ($H_{6exo}$); δ 23.0 ($Me_4$) ↔ δ 2.31 ($Me_4$); δ 21.5 ($Me_3$) ↔ δ 2.58 ($Me_3$); [a] Signals are not resolved. Analysis calculated for $C_{18}H_{26}BCoF_4$: C, 55.70; H, 6.75; found: C, 55.962; H, 6.790. Electrospray MS *m/z* calculated for $C_{18}H_{26}Co$ ($M^+$ - $BF_4$): 301.136649; found: 301.136128 (100%).



**[($\eta^5$-1-*t*-Bu-$C_5H_4$)Co($\eta^5$-3-Ph$C_7H_7$]$^+$ $PF_6^-$ (338).** In the drybox, CpCo($\eta^4$-1-*t*-Bu-$C_5H_5$) (**316**) (0.0645 g, 0.262 mmol) was weighed into a Schlenk flask. The compound was dissolved in degassed dichloromethane (6 mL) and cooled to -40 °C. To the solution was added $HBF_4$•$Et_2O$ (0.042 mL, 1.1 equiv). The color of the red solution turned a deep green upon addition of the acid. After stirring 1 min at -40°C, phenylacetylene (0.082 mL, 3 equiv) was added, changing the color of the solution to a dark red. The solution was slowly warmed with stirring to room temperature overnight. The solvent was removed and the crude residue was extracted with water. A small amount of impure product (about 15 mg, 13%) was precipitated by the addition of $NH_4PF_6$ to the aqueous extracts and tentatively assigned as **338**. $^1$H NMR (300 MHz, $CDCl_3$) δ 8.0-7.0 (m, 5H, $H_{Ph}$), 6.07 (d, J = 9.0 Hz, 2H, $H_{2/4}$), 5.7-5.6 (m, 2H, $H_{1/5}$), 5.52 (br s, 2H, $Cp^t$), 5.39 (br s, 2H, $Cp^t$), 2.6-2.4 (m, 2H, $H_{6endo/7endo}$), 1.3 (m, obscured, 2H, $H_{6exo/7exo}$), 1.09 (s, 9H, *t*-Bu); $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) (phenyl region not reported) δ 6.07 (H2/4) ↔ δ 5.65 ($H_{1/5}$); δ 5.65 ($H_{1/5}$) ↔ δ 2.5 ($H_{6endo/7endo}$), δ 1.3 ($H_{6exo/7exo}$); δ 5.52 ($Cp^t$) ↔ δ 5.39 ($Cp^t$); δ 2.5 ($H_{6endo/7endo}$) ↔ δ 1.3 ($H_{6exo/7exo}$).


t-Bu
Co
316
(i) HBF$_4$•Et$_2$O
Ph—≡—Me
CH$_2$Cl$_2$
-40°C→RT
(ii) NH$_4$PF$_6$, H$_2$O
t-Bu
PF$_6^-$
Co$^+$
Ph
1
7
Me
339

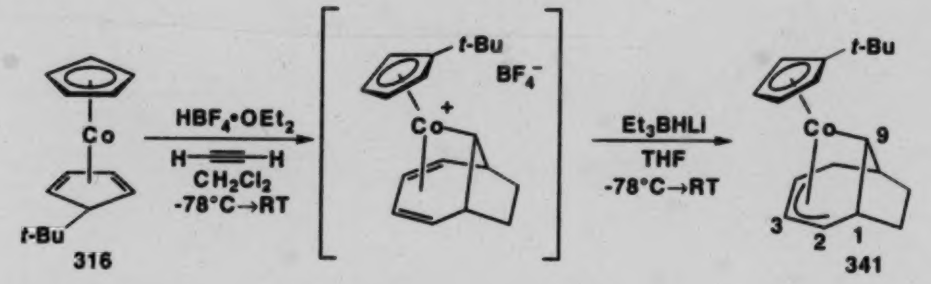
**$[(\eta^5\text{-}1\text{-}t\text{-Bu-}C_5H_4)Co(\eta^5\text{-}4\text{-Me-}3\text{-Ph}C_7H_7]^+ PF_6^-$ (339).** In the drybox, CpCo($\eta^4$-1-*t*-Bu-$C_5H_5$) (**316**) (0.0933 g, 0.379 mmol) was weighed into a Schlenk flask. The compound was dissolved in degassed dichloromethane (10 mL) and cooled to -40 °C. To the solution was added $HBF_4$•$Et_2O$ (0.064 mL, 1.1 equiv). The color of the red solution turned a deep green upon addition of the acid. After stirring 1 min at -40°C, phenylpropyne (0.14 mL, 2 equiv) was added, changing the color of the solution to a dark red. The solution was slowly warmed with stirring to room temperature overnight. The solvent was removed and the crude residue was extracted with water. A small amount of impure product (about 8 mg, 6%) was precipitated by the addition of $NH_4PF_6$ to the aqueous extracts and tentatively assigned as **339**. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.8-7.0 (m, $H_{Ph}$), 6.5-4.8 (series of signals, 7H, obscured by impurities), 3.0-2.7 (m, 1H), 2.13 (s, 3H, Me), 2.4-2.2 (m, 1H), 2.0-1.8 (m, 2H), 1.27 (s, 9H, *t*-Bu), 0.65-0.50 (m, 1H, $H_{6exo}$).


Co
Me
314
HBF$_4$•OEt$_2$
H—≡—H
CH$_2$Cl$_2$
-78°C→RT
Me
BF$_4^-$
Co$^+$
Et$_3$BHLi
THF
-78°C→RT
Me
Co
9
6
5
4
7
3
2
1
8
340

?

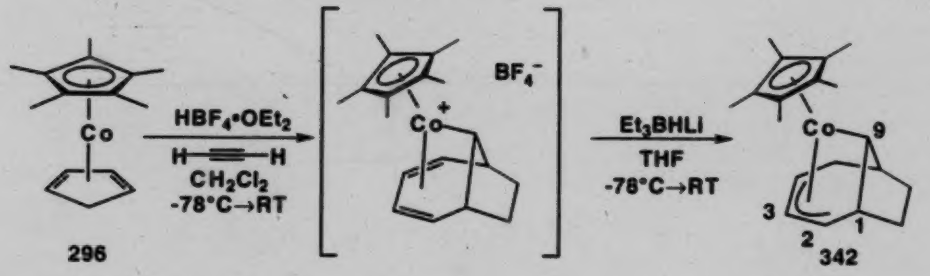
**$(1\text{-Me-}C_5H_4)Co(\eta^1\text{-}\eta^3\text{-bicyclo}[4.2.1]\text{non-2-ene-4,9-diyl})$ (340).** A solution of $C_5H_5Co(1\text{-Me-}C_5H_5)$ (**314**) (61.1 mg, 0.299 mmol) in dichloromethane (6 mL) was cooled to -78°C and $HB_4$•$Et_2O$ (97 µL, 2 equiv) was added. Upon addition, the light orange solution turned dark red-brown. Acetylene was bubbled into the solution for 1 min, causing the solution to lighten slightly to red. The reaction mixture was held at -78°C for 1h, then warmed to room temperature for 1h. The solvent was removed *in vacuo* and the residue was redissolved in tetrahydrofuran (6 mL) and cooled to -78°C. To this solution was added $Et_3BHLi$ (0.9 mL, 1.0 M, THF, 3 equiv) and the solution was allowed to warm slowly to room temperature over 16h. The solvent was removed *in vacuo* and the residue was extracted with pentane. The combined pentane extracts were filtered through a short pad of Celite and the pentane was removed *in vacuo*. A deep red air sensitive oil (55.8 mg, 72%) was obtained. IR (hexane cast, $cm^{-1}$) 2924 (s), 2866 (s), 2824 (m), 1443 (m), 1369 (m), 1319 (w), 1280 (w), 1217 (w), 1157 (w), 1028 (m), 995 (m), 923 (w), 885 (w), 842 (w), 796 (s), 407 (m); $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 4.54 (ddd, $J_{4\text{-}5a}$ = 6.8 Hz, $J_{4\text{-}3}$ = 6.7 Hz, $J_{4\text{-}5b}$ = 1.6 Hz, 1H, $H_4$), 4.45 (br s, 2H, $C_5\underline{H_4}Me$), 4.43-4.40 (m, 1H, $C_5\underline{H_4}Me$), 4.39-4.35 (m, 1H, $C_5H_4Me$), 4.25 (dd, $J_{2\text{-}3}$ = 6.9 Hz, $J_{2\text{-}1}$ = 6.7 Hz, 1H, $H_2$), 3.73 (ddd, $J_{3\text{-}2}$ = 7.0 Hz, $J_{3\text{-}4}$ = 6.6 Hz, $J_{3\text{-}5b}$ = 0.9 Hz, 1H, $H_3$), 2.80 (dddd, $J_{1\text{-}8a}$ = $J_{1\text{-}9}$ = 8.9 Hz, $J_{1\text{-}2}$ = 6.7 Hz, $J_{1\text{-}8b}$ = 5.6 Hz, 1H, $H_1$), 2.63 (dddd, $J_{5a\text{-}5b}$ = 15.5 Hz, $J_{5a\text{-}6}$ = 11.1 Hz, $J_{5a\text{-}4}$ = 6.9 Hz, $J_{5a\text{-}8b}$ = 1.2 Hz, 1H, $H_{5a}$), 2.50-2.40 (m, 1H, $H_6$), 1.82 (s, 3H, $C_5H_4\underline{Me}$), 1.70-1.60 (m, 1H, $H_{8a}$), 1.42 (dd, $J_{9\text{-}1}$ = 9.3 Hz, $J_{9\text{-}6}$ = 6.5 Hz, 1H, $H_9$), 1.34 (br d, dddd by decoupling, $J_{5b\text{-}5a}$ = 15.5 Hz, $J_{5b\text{-}4}$ = $J_{5b\text{-}6}$ = 2.1 Hz, $J_{5b\text{-}3}$ = 0.9 Hz, 1H, $H_{5b}$), 1.20-1.15 (m, 2H, $H_{7a}$ and $H_{7b}$), 1.00-0.90 (m, 1H, $H_{8b}$); $^1H$-$^1H$ GCOSY (300 MHz, $C_6D_6$) $\delta$ 4.54 ($H_4$) ↔ $\delta$ 3.73 ($H_3$), $\delta$ 2.63 ($H_{5a}$), $\delta$ 1.34 ($H_{5b}$); $\delta$ 4.44 ($C_5\underline{H_4}Me$) ↔ $\delta$ 4.37 ($C_5\underline{H_4}Me$); $\delta$ 4.25 ($H_2$) ↔ $\delta$ 3.73 ($H_3$), $\delta$ 2.80 ($H_1$); $\delta$ 3.73 ($H_3$) ↔ $\delta$ 1.34 ($H_{5b}$); $\delta$ 2.80 ($H_1$) ↔ $\delta$ 1.65 ($H_{8a}$), $\delta$ 1.42 ($H_9$), $\delta$ 0.90 ($H_{8b}$); $\delta$ 2.63 ($H_{5a}$) ↔ $\delta$ 2.45 ($H_6$), $\delta$ 1.34 ($H_{5b}$); $\delta$ 2.45 ($H_6$) ↔ $\delta$ 1.42 ($H_9$), $\delta$ 1.34 ($H_{5b}$), $\delta$ 1.17 ($H_{7a/7b}$); $\delta$ 1.65 ($H_{8a}$) ↔ $\delta$ 1.17 ($H_{7a/7b}$), $\delta$ 0.90 ($H_{8b}$); $\delta$ 1.17 ($H_{7a/7b}$) $\delta$ 0.90 ($H_{8b}$); $^{13}C$ NMR (100 MHz, $C_6D_6$) $\delta$ 96.7 (s, $C_5H_4Me$ ring quaternary), 83.5 (d, $^1J_{CH}$ = 155.7 Hz, $C_3$), 82.7$^a$ (d, $^1J_{CH}$ = 175.2 Hz, $\underline{C_5}H_4Me$), 82.5$^a$ (d, $^1J_{CH}$ = 175.2 Hz, $\underline{C_5}H_4Me$), 81.6 (d, $^1J_{CH}$ = 174.2 Hz, $\underline{C_5}H_4Me$), 81.1 (d, $^1J_{CH}$ = 174.0 Hz, $\underline{C_5}H_4Me$), 68.5 (d, $^1J_{CH}$ = 149.4 Hz, $C_4$), 53.4 (d, $^1J_{CH}$ = 162.3 Hz, $C_2$), 48.0 (d, $^1J_{CH}$ = 130.7 Hz, $C_6$), 44.8 (d, $^1J_{CH}$ = 133.6 Hz,

$C_1$), 40.1 (t, $^1J_{CH}$ = 126.1 Hz, $C_5$), 35.7 (t, $^1J_{CH}$ = 127.8 Hz, $C_8$), 33.1 (t, $^1J_{CH}$ = 128.3 Hz, $C_7$), 13.1 (q, $^1J_{CH}$ = 126.7 Hz, $C_5H_4\underline{Me}$), 8.7 (d, $^1J_{CH}$ = 150.4 Hz, $C_9$). $^a$ These signals overlap in gated decoupled spectrum. HMQC (300 MHz, $C_6D_6$) δ 83.5 ($C_3$) ↔ δ 3.73 ($H_3$); δ 82.7 ($\underline{C}_5H_4Me$) ↔ δ 4.44 ($C_5\underline{H}_4Me$); δ 82.5 ($\underline{C}_5H_4Me$) ↔ δ 4.42 ($C_5\underline{H}_4Me$); δ 81.6 ($\underline{C}_5H_4Me$) ↔ δ 4.44 ($C_5\underline{H}_4Me$); δ 81.1 ($\underline{C}_5H_4Me$) ↔ δ 4.37 ($C_5\underline{H}_4Me$); δ 68.5 ($C_4$) ↔ δ 4.54 ($H_4$); δ 53.4 ($C_2$) ↔ δ 4.25 ($H_2$); δ 48.0 ($C_6$) ↔ δ 2.45 ($H_6$); δ 44.8 ($C_1$) ↔ δ 2.80 ($H_1$); δ 40.1 ($C_5$) ↔ δ 2.63 ($H_{5a}$), δ 1.34 ($H_{5b}$); δ 35.7 ($C_8$) ↔ δ 1.65 ($H_{8a}$), δ 0.90 ($H_{8b}$); δ 33.1 ($C_7$) ↔ δ 1.17 ($H_{7a/7b}$); δ 13.1 ($C_5H_4\underline{Me}$) ↔ δ 1.82 ($C_5H_4\underline{Me}$); δ 8.7 ($C_9$) ↔ δ 1.42 ($H_9$); HMBC (300 MHz, $C_6D_6$) δ 96.7 ($C_5H_4Me$ ring quaternary) ↔ δ 4.44 ($C_5H_4\underline{Me}$), δ 1.82 ($C_5H_4\underline{Me}$); δ 83.5 ($C_3$) ↔ δ 4.25 ($H_2$), δ 2.80 ($H_1$), δ 2.63 ($H_{5a}$), δ 2.45 ($H_6$), δ 1.34 ($H_{5b}$); δ 68.5 ($C_4$) ↔ δ 4.25 ($H_2$), δ 3.73 ($H_3$), δ 2.63 ($H_{5a}$), δ 2.45 ($H_6$), δ 1.34 ($H_{5b}$); δ 53.4 ($C_2$) ↔ δ 4.54 ($H_4$), δ 3.73 ($H_3$), δ 2.80 ($H_1$), δ 1.65 ($H_{8a}$), δ 1.42 ($H_9$), δ 0.90 ($H_{8b}$); δ 48.0 ($C_6$) ↔ δ 4.54 ($H_4$), δ 2.80 ($H_1$), δ 2.63 ($H_{5a}$), δ 1.65 ($H_{8a}$), δ 1.34 ($H_{5b}$), δ 1.17 ($H_{7a/7b}$); δ 44.8 ($C_1$) ↔ δ 4.25 ($H_2$), δ 3.73 ($H_3$), δ 0.90 ($H_{8a}$), δ 1.17 ($H_{7a/7b}$); δ 40.1 ($C_5$) ↔ δ 3.73 ($H_3$), δ 1.42 ($H_9$), δ 1.17 ($H_{7a/7b}$); δ 33.1 ($C_7$) ↔ δ 2.63 ($H_{5a}$), δ 2.45 ($H_6$), δ 1.34 ($H_{5b}$), δ 0.90 ($H_{8a}$); δ 8.7 ($C_9$) ↔ δ 4.25 ($H_2$), δ 2.80 ($H_1$), δ 2.45 ($H_6$), δ 1.65 ($H_{8a}$), δ 1.34 ($H_{5b}$), δ 1.17 ($H_{7a/7b}$), δ 0.90 ($H_{8a}$). MS *m/z* calculated for $C_{15}H_{19}Co$ ($M^+$): 258.08188; found: 258.08187 (100%).

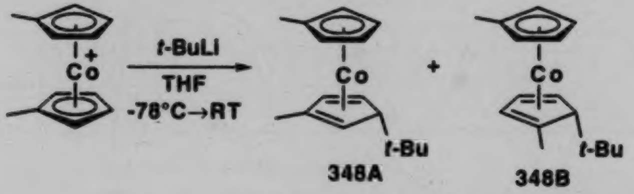


**($t$-Bu-$C_5H_4$)Co($\eta^1$-$\eta^3$-bicyclo[4.2.1]non-2-ene-4,9-diyl) (341).** A solution of $C_5H_5Co$(t-Bu-$C_5H_5$) **(316)** (156.7 mg, 0.636 mmol) in dichloromethane (16 mL) was cooled to -78°C and $HB_4 \bullet Et_2O$ (206 µL, 2 equiv) was added. Upon addition, the light orange solution turned dark red-brown. Acetylene was bubbled into the solution for 1 min, causing the color of the solution to change to dark red. The reaction mixture was held at -78°C for 1h, then warmed to room temperature for 1h. The solvent was removed *in vacuo* and the residue was redissolved in tetrahydrofuran (16 mL) and cooled to -78°C. To this solution was added $Et_3BHLi$ (1.9 mL, 1.0 M, THF, 3 equiv) and the solution was allowed to warm slowly to room temperature over 16h. The solvent was removed *in vacuo* and the residue was extracted with pentane. The combined pentane extracts were filtered through a short pad of Celite and the pentane was removed *in vacuo*. A deep red air sensitive oil (154.3 mg, 81%) was obtained. IR (hexane cast, $cm^{-1}$) 2932 (s), 2866 (s), 1482 (m), 1458 (m), 1360 (m), 1318 (w), 1274 (m), 1198 (w), 1151 (w), 1108 (m), 1040 (m), 1016 (m), 997 (m), 910 (m), 885 (w), 844 (w), 798 (s), 668 (w), 405 (s); $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 4.69 (ddd, $J_{4\text{-}3}$ = 6.9 Hz, $J_{4\text{-}5a}$ = 6.8 Hz, $J_{4\text{-}5b}$ = 1.8 Hz, 1H, $H_4$), 4.65 (narrow m, 1H, $Cp^t$), 4.52 (narrow m, 1H, $Cp^t$), 4.38 (dd, $J_{2\text{-}3}$ = 8.0 Hz, $J_{2\text{-}1}$ = 7.0 Hz, 1H, $H_2$), 4.37 (narrow m, 1H, $Cp^t$), 4.28 (narrow m, 1H, $Cp^t$), 3.81 (ddd, $J_{3\text{-}2}$ = 8.0 Hz, $J_{3\text{-}4}$ = 6.6 Hz, $J_{3\text{-}5b}$ = 0.7 Hz, 1H, $H_3$), 2.77 (m, dddd by decoupling, $J_{1\text{-}9} = J_{1\text{-}8a}$ = 9.1 Hz, $J_{1\text{-}8b}$ = 5.6 Hz, $J_{1\text{-}2} \approx$ 7 Hz, 1H, $H_1$), 2.65 (ddd, $J_{5a\text{-}5b}$ = 15.5 Hz, $J_{5a\text{-}6}$ = 11.2 Hz, $J_{5a\text{-}4}$ = 7.0 Hz, 1H, $H_{5a}$), 2.43 (m, dddd by decoupling, $J_{6\text{-}5a}$ = 11.2 Hz, $J_{6\text{-}9}$ = 6.2 Hz, $J_{6\text{-}5b}$ = small, $J_{6\text{-}8a}$ = small, 1H, $H_6$), 1.73 (m, dddd by decoupling, $J_{8a\text{-}8b}$ = 12.3 Hz, $J_{8a\text{-}7} = J_{8a\text{-}1}$ = 8.1 Hz, $J_{8a\text{-}6} < 1$ Hz, 1H, $H_{8a}$), 1.59 (dd, $J_{9\text{-}1}$ = 9.3 Hz, $J_{9\text{-}6}$ = 6.2 Hz, 1H, $H_9$), 1.3 (br d, $J \approx$ 13.5 Hz, 1H, $H_{5b}$), 1.24 (s, 9H, *t*-Bu), 1.15-1.05 (m, 2H, $H_{7a/7b}$), 1.0-0.9 (m, 1H, $H_{8b}$); $^1H$-$^1H$ GCOSY (300 MHz, $C_6D_6$) $\delta$ 4.69 ($H_4$) ↔ $\delta$ 3.81 ($H_3$), $\delta$ 2.65 ($H_{5a}$), $\delta$ 1.3 ($H_{5b}$); $\delta$ 4.65 ($Cp^t$) ↔ $\delta$ 4.52 ($Cp^t$), $\delta$ 4.37 ($Cp^t$), $\delta$ 4.28 ($Cp^t$); $\delta$ 4.52 ($Cp^t$) ↔ $\delta$ 4.37 ($Cp^t$), $\delta$ 4.28 ($Cp^t$); $\delta$ 4.37 ($Cp^t$) ↔ $\delta$ 4.28 ($Cp^t$); $\delta$ 4.38 ($H_2$) ↔ $\delta$ 3.81 ($H_3$), $\delta$ 2.77 ($H_1$); $\delta$ 3.81 ($H_3$) ↔ $\delta$ 1.3 (w, $H_{5b}$); $\delta$ 2.77 ($H_1$) ↔ $\delta$ 1.73 ($H_{8a}$), $\delta$ 1.59 ($H_9$), $\delta$ 0.95 ($H_{8b}$); $\delta$ 2.65 ($H_{5a}$) ↔ $\delta$ 2.43 ($H_6$), $\delta$ 1.3 ($H_{5b}$); $\delta$ 2.43 ($H_6$) ↔ $\delta$ 1.59 ($H_9$), $\delta$ 1.3 ($H_{5b}$), $\delta$ 1.1 ($H_{7a/7b}$); $\delta$ 1.73 ($H_{8a}$) ↔ $\delta$ 1.1 ($H_{7a/7b}$), $\delta$ 0.95 ($H_{8b}$); $\delta$ 1.1 ($H_{7a/7b}$) ↔ $\delta$ 0.95 ($H_{8b}$);

$^{13}C$ NMR (100 MHz, $C_6D_6$) $\delta$ 113.3 (s, Cp$^t$ ring quaternary), 83.1 (d, $^1J_{CH}$ = 157.5 Hz, $C_3$), 81.2 (d, $^1J_{CH}$ = 171.2 Hz, *t*-Bu-$\underline{C}_5H_4$), 80.8 (d, $^1J_{CH}$ = 171.2 Hz, *t*-Bu-$\underline{C}_5H_4$), 80.3 (d, $^1J_{CH}$ = 173.6 Hz, *t*-Bu-$\underline{C}_5H_4$), 79.9 (d, $^1J_{CH}$ = 174.4 Hz, *t*-Bu-$\underline{C}_5H_4$), 67.1 (d, $^1J_{CH}$ = 147.5 Hz, $C_4$), 54.1 (d, $^1J_{CH}$ = 156.5 Hz, $C_2$), 49.0 (d, $^1J_{CH}$ = 130.0 Hz, $C_6$), 44.8 (d, $^1J_{CH}$ = 127.6 Hz, $C_1$), 40.0 (t, $^1J_{CH} \approx$ 120 Hz, $C_5$), 35.9 (t, $^1J_{CH}$ = 131.6 Hz, $C_8$), 33.1 (t, $^1J_{CH}$ = 127.5 Hz, $C_7$), 31.7 (q, $^1J_{CH}$ = 125.5 Hz, *t*-Bu), 6.5 (d, $^1J_{CH}$ = 146.8 Hz, $C_9$); HMQC (300 MHz, $C_6D_6$) $\delta$ 83.1 ($C_3$) $\leftrightarrow$ $\delta$ 3.81 ($H_3$); $\delta$ 81.2 (*t*-Bu-$\underline{C}_5H_4$) $\leftrightarrow$ $\delta$ 4.52 (*t*-Bu-$C_5\underline{H}_4$); $\delta$ 80.8 (*t*-Bu-$\underline{C}_5H_4$) $\leftrightarrow$ $\delta$ 4.28 (*t*-Bu-$C_5\underline{H}_4$); $\delta$ 80.3 (*t*-Bu-$\underline{C}_5H_4$) $\leftrightarrow$ $\delta$ 4.65 (*t*-Bu-$C_5\underline{H}_4$); $\delta$ 79.9 (*t*-Bu-$\underline{C}_5H_4$) $\leftrightarrow$ $\delta$ 4.37 (*t*-Bu-$C_5\underline{H}_4$); $\delta$ 67.1 ($C_4$) $\leftrightarrow$ $\delta$ 4.69 ($H_4$); $\delta$ 54.1 ($C_2$) $\leftrightarrow$ $\delta$ 4.38 ($H_2$); $\delta$ 49.0 ($C_6$) $\leftrightarrow$ $\delta$ 2.43 ($H_6$); $\delta$ 44.8 ($C_1$) $\leftrightarrow$ $\delta$ 2.77 ($H_1$); $\delta$ 40.0 ($C_5$) $\leftrightarrow$ $\delta$ 2.65 ($H_{5a}$), $\delta$ 1.30 ($H_{5b}$); $\delta$ 35.9 ($C_8$) $\leftrightarrow$ $\delta$ 1.73 ($H_{8a}$), $\delta$ 0.9 ($H_{8b}$); $\delta$ 33.1 ($C_7$) $\leftrightarrow$ $\delta$ 1.10[a] ($H_{7a/7b}$); $\delta$ 31.7 (*t*-$\underline{Bu}$-$C_5H_4$) $\leftrightarrow$ $\delta$ 1.24 (*t*-$\underline{Bu}$-$C_5H_4$); $\delta$ 6.5 ($C_9$) $\leftrightarrow$ $\delta$ 1.59 ($H_9$). [a] This correlation is not resolved from the large *t*-Bu correlation. MS *m/z* calculated for $C_{18}H_{25}Co$ ($M^+$): 300.12881; found: 300.12933 (55%). MS *m/z* calculated for $C_{14}H_{16}Co$ ($M^+$- *t*-Bu): 243.05840 found: 243.05860 (100%).

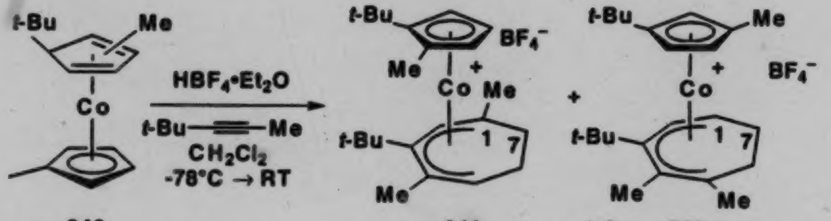


**($C_5Me_5$)Co($\eta^1$-$\eta^3$-bicyclo[4.2.1]non-2-ene-4,9-diyl) (342).** A solution of Cp*Co($C_5H_6$) (**296**) (24.6 mg, 0.0945 mmol) in dichloromethane (3 mL) was cooled to -78°C and $HB_4$•$Et_2O$ (31 µL, 2 equiv) was added. Upon addition of the acid, the light orange solution turned dark green. Acetylene was bubbled into the solution for 1 min, causing the solution to change color to red. The reaction mixture was held at -78°C for 1h, then warmed to room temperature for 1h. The solvent was removed *in vacuo* and the residue was redissolved in tetrahydrofuran (3 mL) and cooled to -78°C. To this solution was added $Et_3BHLi$ (0.28 mL, 1.0 M, THF, 3 equiv) and the solution was allowed to warm slowly to room temperature over 16h. The solvent was removed *in vacuo* and the residue was extracted with pentane. The combined pentane extracts were filtered through a short pad of Celite and the pentane was removed *in vacuo*. An orange air sensitive solid (9.5 mg, 32%) was obtained. IR (hexane cast, $cm^{-1}$) 2910 (s), 2854 (s), 2820 (m), 1480 (w), 1442 (w), 1380 (m), 1260 (m), 1155 (w), 1088 (m), 1027 (m), 884 (w), 800 (m), 668 (m), 424 (m), 410 (m); $^1H$ NMR (400 MHz, $C_6D_6$) $\delta$ 3.69 (dd, $J$ = 8.0, 7.0 Hz, 1H, $H_4$), 3.48 (dd, $J$ = 6.9, 6.8 Hz, 1H, $H_2$), 3.15 (dd, $J$ = 7.7, 7.3 Hz, 1H, $H_3$), 2.85-2.75 (m, 1H, $H_1$), 2.50 (ddd, $J$ = 17.5, 11.0, 6.4 Hz, 1H, $H_{5a}$), 2.51-2.40 (m, 1H, $H_6$), 1.7-1.6 (m, 1H, obscured by Cp*, 1H, $H_{8a}$), 1.61 (s, 15H, $C_5\underline{Me_5}$), 1.45 (br d, $J$ = 14.3 Hz, 1H, $H_{5b}$), 1.25-1.15 (m, 2H, $H_{7a/7b}$), 1.05-0.95 (m, 1H, $H_{8b}$), 0.58 (dd, $J$ = 9.2, 6.1 Hz, 1H, $H_9$); $^{13}C$ NMR[a] (100 MHz, $C_6D_6$) $\delta$ 90.5 ($\underline{C_5}Me_5$), 88.1 ($C_3$), 71.9 ($C_4$), 55.8 ($C_2$), 46.8 ($C_6$), 44.9 ($C_1$), 40.3 ($C_5$), 35.6 ($C_8$), 33.8 ($C_7$), 9.7 ($C_5\underline{Me_5}$), 9.5 ($C_1$). [a]Assignments are based on comparison with the analogous *t*-BuCp and MeCp systems. MS *m/z* calculated for $C_{19}H_{27}Co$ ($M^+$): 314.14447; found: 314.14443 (100%).



**[($\eta^5$-1-Me-$C_5H_4$)Co($\eta^4$-2-Me-5-*t*-Bu-$C_5H_4$] (348A) and [($\eta^5$-1-Me-$C_5H_4$)Co($\eta^4$-1-Me-5-*t*-Bu-$C_5H_4$] (348B).** To a suspension of $(1\text{-}MeC_5H_4)_2Co^+$ $PF_6^-$ (6.5 g, 17.9 mmol) in tetrahydrofuran (100 mL) at -78°C was added *t*-BuLi (10.6 mL, 1.7 M, pentane, 1.01 equiv). The yellow suspension quickly turned into a red solution. After stirring at -78°C overnight, allowing the solution to warm to room temperature, the solvent was removed *in vacuo* and the residue was extracted with hexane under nitrogen. The extracts were filtered through Celite and the hexane was removed. A red oil (4.3227 g, 88%) remained. By $^1H$ NMR spectroscopy, an approximately 2:1 mixture of isomers was obtained. IR (hexane cast, $cm^1$) 3081 (w), 3050 (w), 2954 (s), 2899 (s), 2864 (s), 1474 (m), 1461 (m), 1415 (w), 1389 (m), 1374 (m), 1361 (s), 1315 (m), 1252 (w), 1223 (m), 1190 (w), 1033 (m), 1190 (w), 1033 (m), 963 (w), 922 (w), 850 (m), 800 (m), 558 (w), 508 (w), 456 (w), 418 (m); $^1H$ NMR (300 MHz, $C_6D_6$) (select data only) major isomer: δ 1.82 (s, 3H, Me), 1.18 (s, 3H, Me), 0.64 (s, 9H, *t*-Bu). Minor isomer: δ 2.01 (s, 3H, Me), 1.71 (s, 3H, Me), 0.57 (s, 9H, *t*-Bu). MS *m/z* calculated for $C_{16}H_{22}Co$ ($M^+$ -H): 273.10535; found: 273.10490 (15%). MS *m/z* calculated for $C_{12}H_{14}Co$ ($M^+$ - *t*-Bu): 217.04276; found: 217.04247 (100%).

**General note** for the seven-membered ring compounds prepared using the *t*-Bu-MeC$_5$H$_4$ template. Unless stated otherwise, yields are given for the isomeric mixture of seven-membered ring products after crude chromatographic separation to remove non-seven-membered ring impurities. However, only small amounts of any given isomer can be obtained in a pure state by crystallization or slow chromatography. Most of the material balance still exists as a mixture of isomers. For this reason, isolated yields of the individual isomers are not given, as they are somewhat variable and do not reflect the true efficiency of this reaction.



348 349 1:2 350

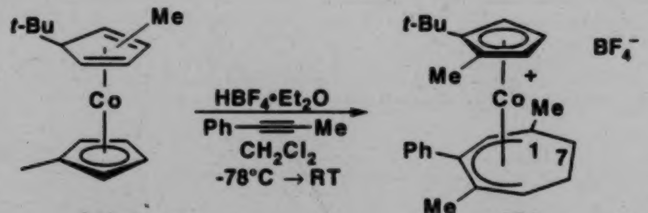
**[(*t*-Bu-Me-C$_5$H$_3$)Co(3-*t*-Bu-1,4-Me$_2$C$_7$H$_6$)]$^+$ BF$_4^-$ (349) and [(*t*-Bu-Me-C$_5$H$_3$)Co(3-*t*-Bu-4,5-Me$_2$C$_7$H$_6$)]$^+$ BF$_4^-$ (350)**. In the drybox, a flask was charged with Cp'Co(Cp''H)

(**348**) (0.1078 g, 0.3930 mmol) and removed to the Schlenk line, where dichloromethane (10 mL) was added. The solution was cooled to -78 °C and 4,4-dimethyl-2-pentyne (0.37 mL, 7 equiv) was added. Upon addition of $HBF_4•Et_2O$ (64 µL, 1.1 equiv), the color turned to green. After 2 h at -78 °C, the solution had not changed color. Warming slowly to room temperature gave a red solution. Removal of all volatile material gave a deep red residue. The compound was purified by flash chromatography (silica gel) using 5% methanol-dichloromethane. After a red band was collected and the solvent was removed, there remained a red residue. Attempted recrystallization from chloroform/diethyl ether only gave oils, which later solidified upon drying *in vacuo*, to give an orange-red solid (0.1560 g, 87%). This crude material was shown to be at least two compounds, a major and minor complex in about a 2:1 ratio by $^1$H NMR spectroscopy; however, extraction with ethyl acetate left behind a light orange powder. This powder was recrystallized from dichloromethane/ethyl acetate/diethyl ether, and shown to be a single product: the 1,3,4-cycloheptadienyl isomer **349**. The ethyl acetate soluble portion contained a mixture of two compounds, including the "insoluble" product. By $^1$H NMR spectroscopy, the other product appeared to be a positional isomer of the 1,3,4-compound **349**. Further chromatography (silica gel, 2% methanol/dichloromethane allowed enrichment of the ethyl acetate soluble isomer, which was identified by $^1$H NMR as the 3,4,5-isomer **350**. Recrystallization of **350** from dichloromethane/ethyl acetate/diethyl ether yielded crystals suitable for X-ray diffractrion analysis. For full data on this crystal structure, request report # JMS9807 from the Structure Determination Laboratory at the University of Alberta Department of Chemistry. Data for ethyl acetate insoluble 1,3,4-isomer **349**: IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3096 (w), 2975 (m), 2874 (m), 1482 (m), 1457 (m), 1423 (w), 1398 (w), 1382 (m), 1367 (m), 1313 (w), 1281 (w), 1238 (w), 1186 (w), 1088 (s), 1058 (s), 1035 (s), 851 (m), 520 (w); $^1$H NMR (400 MHz, $CDCl_3$) δ 5.30 (s, 1H, $H_2$), 5.11 (t, $J$ = 2.8 Hz, 1H, Cp$'^{t}$), 4.91 (t, $J$ = 2.4 Hz, 1H, Cp$'^{t}$), 4.80 (dd, $J_{5\text{-}6endo}$ = 8.3 Hz, $J_{5\text{-}6exo}$ = 4.6 Hz, 1H, $H_5$), 4.37 (t, $J$ = 2.5 Hz, 1H, Cp$'^{t}$), 2.57 (ddd, $J_{7endo\text{-}7exo}$ = 17.7 Hz, $J_{7exo\text{-}6exo}$ =

10.8 Hz, $J_{7endo\text{-}6endo}$ = 9.0 Hz, 1H, H$_{7endo}$), 2.37 (s, 3H, Me$_4$), 2.25 (s, 3H, Cp$'^{t}$ Me), 1.83 (s, 3H, Me$_1$), 1.8-1.7$^{a}$ (m, $J_{7exo\text{-}7endo}$ = 17.7 Hz, $J_{7exo\text{-}6exo}$ = 9.7 Hz, 1H, H$_{7exo}$), 1.7-1.6$^{a}$ (m, $J_{6endo\text{-}6exo}$ = 13.1 Hz, $J_{6endo\text{-}7endo}$ = 9.0 Hz, $J_{6endo\text{-}5}$ = 8.3 Hz, 1H, H$_{6endo}$), 1.64 (s, 9H, Cp$'^{t}$ *t*-Bu), 1.42 (s, 9H, C$_3$ *t*-Bu), 0.20 (m, dddd by decoupling, $J_{6exo\text{-}6endo}$ = 12.5 Hz, $J_{6exo\text{-}7endo}$ = 12.5 Hz, $J_{6exo\text{-}7exo}$ = 9.7 Hz, $J_{6exo\text{-}5}$ = 4.6 Hz, 1H, H$_{6exo}$). $^{a}$Other *J* values not determined. $^1$H-$^1$H GCOSY (300 MHz, CDCl$_3$) δ 5.30 (H$_2$) ↔ δ 2.37 (w, Me$_4$), δ 1.83 (Me$_1$), δ 1.73 (H$_{7exo}$); δ 5.11 (Cp$'^{t}$) ↔ δ 4.91 (Cp$'^{t}$), δ 4.37 (Cp$'^{t}$); δ 4.91 (Cp$'^{t}$) ↔ δ 4.37 (Cp$'^{t}$); δ 4.80 (H$_5$) ↔ δ 1.65 (H$_{6endo}$), δ 0.20 (H$_{6exo}$); δ 2.57 (H$_{7endo}$) ↔ δ 1.73 (H$_{7exo}$), δ 1.65 (H$_{6endo}$), δ 0.20 (H$_{6exo}$); 1.73 (H$_{7exo}$) ↔ δ 0.20 (H$_{6exo}$); 1.65 (H$_{6endo}$) ↔ δ 0.20 (H$_{6exo}$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 130.2 (s, C$_3$), 116.0 (s, Cp$'^{t}$ ring quaternary), 106.4 (s, C$_1$), 105.5 (s, C$_4$), 100.3 (s, Cp$'^{t}$ ring quaternary), 90.4 (d, $^1J_{CH}$ = 163.3 Hz, C$_2$), 89.1 (d, $^1J_{CH}$ = 178.9 Hz, Cp$'^{t}$), 85.4 (d, $^1J_{CH}$ = 177.8 Hz, Cp$'^{t}$), 82.9 (d, $^1J_{CH}$ = 182.9 Hz, Cp$'^{t}$), 79.3 (d, $^1J_{CH}$ = 158.6 Hz, C$_5$), 44.7 (t, $^1J_{CH}$ = 127.7 Hz, C$_7$), 37.1 (s, Cp$'^{t}$ *t*-Bu quaternary), 32.4 (s, C$_3$ *t*-Bu quaternary), 32.3 (q, $^1J_{CH}$ = 127.2 Hz, Cp$'^{t}$ *t*-Bu), 30.3 (q, $^1J_{CH}$ = 127.0 Hz, C$_3$ *t*-Bu), 29.4 (q, $^1J_{CH}$ = 129.3 Hz, Me$_1$), 25.5$^{a}$ (q, $^1J_{CH}$ = 129.0 Hz, Me$_4$), 25.0$^{a}$ (t, $^1J_{CH}$ = 129.0 Hz, C$_6$), 13.2 (q, $^1J_{CH}$ = 129.3 Hz, Cp$'^{t}$ Me). $^{a}$Overlap in gated spectrum. HMQC (300 MHz, CDCl$_3$) δ 90.4 (C$_2$) ↔ δ 5.30 (H$_2$); δ 89.1 (Cp$'^{t}$) ↔ δ 4.91 (Cp$'^{t}$); δ 85.4 (Cp$'^{t}$) ↔ δ 4.37 (Cp$'^{t}$); δ 82.9 (Cp$'^{t}$) ↔ δ 5.11 (Cp$'^{t}$); δ 79.3 (C$_5$) ↔ δ 4.80 (H$_5$); δ 44.7 (C$_7$) ↔ δ 2.57 (H$_{7endo}$), δ 1.75 (H$_{7exo}$); δ 32.3 (Cp$'^{t}$ *t*-Bu) ↔ δ 1.64 (Cp$'^{t}$ *t*-Bu); δ 30.3 (C$_3$ *t*-Bu) ↔ δ 1.42 (C$_3$ *t*-Bu); δ 29.4 (Me$_1$) ↔ δ 1.83 (Me$_1$); δ 25.5 (Me$_4$) ↔ δ 2.37 (Me$_4$); δ 25.0 (C$_6$) ↔ δ 1.65 (H$_{6endo}$), δ 0.20 (H$_{6exo}$); δ 13.2 (Cp$'^{t}$ Me) ↔ δ 2.25 (Cp$'^{t}$ Me); HMBC (300 MHz, CDCl$_3$) δ 130.2 (C$_3$) ↔ δ 4.80 (H$_5$), δ 2.37 (Me$_4$); δ 116.0 (Cp$'^{t}$) ↔ δ 5.11 (Cp$'^{t}$) δ 4.91 (Cp$'^{t}$), δ 4.37 (Cp$'^{t}$), δ 2.25 (Cp$'^{t}$ Me); δ 106.4 (C$_1$) ↔ δ 2.57 (H$_{7endo}$), 1.83 (Me$_1$); δ 105.5 (C$_4$) ↔ δ 5.30 (H$_2$), δ 2.37 (Me$_4$), δ 0.20 (H$_{6exo}$); δ 100.3 (Cp$'^{t}$) ↔ δ 5.11 (Cp$'^{t}$), δ 4.91 (Cp$'^{t}$), δ 4.37 (Cp$'^{t}$), δ 2.25 (Cp$'^{t}$ Me); δ 90.4 (C$_2$) ↔ δ 2.57 (H$_{7exo}$), δ 1.73 (H$_{7exo}$); δ 89.1 (Cp$'^{t}$) ↔ δ 5.11 (Cp$'^{t}$), δ 4.37 (Cp$'^{t}$), δ 2.25 (Cp$'^{t}$ Me); δ 85.4 (Cp$'^{t}$) ↔ δ 5.11 (Cp$'^{t}$), δ 4.91 (Cp$'^{t}$); δ 82.9

(Cp'$^t$) ↔ δ 4.91 (Cp'$^t$), δ 4.37 (Cp'$^t$); δ 79.3 (C$_5$) ↔ δ 2.37 (Me$_4$); δ 44.7 (C$_7$) ↔ δ 4.80 (H$_5$), δ 1.73 (H$_{7exo}$), δ 0.20 (H$_{6exo}$); δ 37.1 (Cp'$^t$ *t*-Bu) ↔ δ 5.11 (Cp'$^t$), δ 1.64 (Cp'$^t$ *t*-Bu); δ 32.4/32.3$^a$ (*t*-Bu quaternaries) ↔ δ 1.64 (Cp'$^t$ *t*-Bu), δ 1.42 (C$_3$ *t*-Bu); δ 30.3 (C$_3$ *t*-Bu) ↔ δ 1.42 (C$_3$ *t*-Bu); δ 25.5/25.0$^a$ (Me/C$_6$) ↔ δ 4.80 (H$_5$). $^a$Resolution insufficient to separate signals. Analysis calculated for $C_{23}H_{36}BCoF_4$: C, 60.28; H, 7.92; found: C, 60.173; H, 7.983.

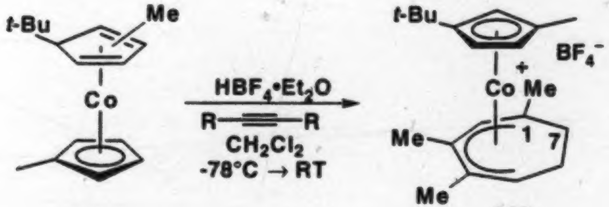
Data for 3,4,5-isomer **350**: $^1$H NMR (360 MHz, CDCl$_3$) δ 5.27 (t, $J$ = 2.7 Hz, Cp'$^t$), 5.16 (t, $J$ = 2.0 Hz, 1H, Cp'$^t$), 5.05-4.95 (m, 1H, H$_1$), 4.89 (d, $J \approx$ 8.0 Hz, 1H, H$_2$), 4.87 (t, $J$ = 2.7 Hz, 1H, Cp'$^t$), 3.03 (dddd, $J_{7endo\text{-}7exo}$ = 17.7 Hz, $J_{7endo\text{-}6exo}$ = 12.8 Hz, $J_{7endo\text{-}6endo}$ = 6.6 Hz, $J_{7endo\text{-}1}$ = 2.4 Hz, 1H, H$_{7endo}$), 2.59 (s, 3H, Me), 2.47 (s, 3H, Me), 2.37-2.27 (m, 1H, H$_{7exo}$), 1.93 (s, 3H, Me), 1.61 (s, 9H, *t*-Bu), 1.14 (s, 9H, *t*-Bu), 1.05 (ddd, $J_{6endo\text{-}6exo}$ = 11.5 Hz, $J_{6endo\text{-}7endo}$ = 6.2 Hz, $J_{6endo\text{-}7exo}$ = 1.9 Hz, 1H, H$_{6endo}$), -0.19 (ddd, $J_{6exo\text{-}6endo}$ = $J_{6exo\text{-}7endo}$ = 12.6 Hz, $J_{6exo\text{-}7exo}$ = 4.6 Hz, 1H, H$_{6exo}$).



**348** **351**

**[(*t*-Bu-Me-C$_5$H$_3$)Co(1,4-Me$_2$-3-PhC$_7$H$_6$)]$^+$ BF$_4^-$ (351).** In the drybox, a flask was charged with Cp'Co(Cp''H) (**348**) (0.0848 g, 0.309 mmol) and removed to the Schlenk line, where dichloromethane (9 mL) was added. The solution was cooled to -78 °C and 1-phenylpropyne (0.19 mL, 5 equiv) was added. Upon addition of HBF$_4$•Et$_2$O (50 µL, 1.1 equiv), the color turned to green. Allowing the solution to warm to room temperature gave a deep red solution. Removal of all volatile material gave a dark oily residue. The compound was purified by flash chromatography (silica gel) using 5% methanol-dichloromethane. After a red band was collected and the solvent was removed, there remained a red residue (0.073 g, 49%). This material was shown by $^1$H NMR spectroscopy to contain a single major product, although minor impurities are present. IR ($CDCl_3$ cast, $cm^{-1}$) 3104 (w), 2966 (s), 2874 (m), 2262 (w), 2171 (w), 1717 (w), 1652 (w), 1483 (m), 1456 (s), 1381 (m), 1262 (m), 1221 (m), 1188 (m), 1055 (s), 918 (s), 857 (m), 766 (m), 728 (s), 706 (s), 680 (m), 647 (w), 521 (m); $^1H$ NMR (360 MHz, $CDCl_3$) $\delta$ 7.79 (d, $J$ = 7.2 Hz, 2H, $H_{Ph}$), 7.54 (t, $J$ = 7.3 Hz, 2H, $H_{Ph}$), 7.47 (t, $J$ = 7.3 Hz, 1H, $H_{Ph}$), 5.52 (s, 1H, $H_2$), 5.39 (t, $J$ = 2.3 Hz, 1H, $Cp'^{t}$), 5.10 (dd, $J_{5\text{-}6endo}$ = 8.1 Hz, $J_{5\text{-}6exo}$ = 4.4 Hz, 1H, $H_5$), 4.78 (t, $J$ = 2.8 Hz, 1H, $Cp'^{t}$), 4.36 (t, $J$ = 2.2 Hz, 1H, $Cp'^{t}$), 2.65 (m, apparent quintet, $J$ = 18.9, 9.2, 9.2 Hz, 1H, $H_{7endo}$), 2.20 (s, 3H, Me), 2.16 (s, 3H, Me), 2.05-1.90 (m, 1H, $H_{6endo}$), 1.90-1.80 (m, 1H, $H_{7exo}$), 1.84 (s, 3H, Me), 1.42 (m, dddd by decoupling, $J$ = 13.9, 9.9, 6.0, 5.5 Hz, 1H, $H_{6exo}$); $^1H$-$^1H$ GCOSY (300 MHz, $CDCl_3$) $\delta$ 7.79 ($H_{Ph}$) ↔ $\delta$ 7.54 ($H_{Ph}$); $\delta$ 5.52 ($H_2$) ↔ $\delta$ 2.16 (Me), $\delta$ 1.85 ($H_{7exo}$); $\delta$ 5.39 ($Cp'^{t}$) ↔ $\delta$ 4.78 ($Cp'^{t}$), $\delta$ 4.36 ($Cp'^{t}$); $\delta$ 5.10 ($H_5$) ↔ $\delta$ 1.95 ($H_{6endo}$), $\delta$ 0.61 ($H_{6exo}$); $\delta$ 4.78 ($Cp'^{t}$) ↔ $\delta$ 4.36 ($Cp'^{t}$); $\delta$ 2.65 ($H_{7endo}$) ↔ $\delta$ 1.95 ($H_{6endo}$), $\delta$ 1.85 ($H_{7exo}$), $\delta$ 0.61 ($H_{6exo}$); $\delta$ 1.95 ($H_{6endo}$) ↔ $\delta$ 1.85 ($H_{7exo}$), $\delta$ 0.61 ($H_{6exo}$); $\delta$ 1.85 ($H_{7exo}$) ↔ $\delta$ 0.61 ($H_{6exo}$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 136.0 (s, $C_{Ph}$), 129.7 (d, $^1J_{CH}$ = 152.1 Hz, $C_{Ph}$), 129.3 (d, $^1J_{CH}$ = 161.5 Hz, $C_{Ph}$), 116.6 (s, $C_{quaternary}$), 115.5 (s, $C_{quaternary}$), 109.0 (s, $C_{quaternary}$), 107.8 (s, $C_{quaternary}$), 100.3 (s, $C_{quaternary}$), 95.4 (d, $^1J_{CH}$ = 164.1 Hz, $C_2$), 88.8 (d, $^1J_{CH}$ = 182.5 Hz, $Cp'^{t}$), 86.0 (d, $^1J_{CH}$ = 182.7 Hz, $Cp'^{t}$), 85.3 (d, $^1J_{CH}$ = 178.8 Hz, $Cp'^{t}$), 80.2 (d, $^1J_{CH}$ = 158.8 Hz, $C_5$), 44.5 (t, $^1J_{CH}$ = 130.8 Hz, $C_7$), 32.2 (s, *t*-Bu quaternary), 30.3 (q, $^1J_{CH}$ = 127.1 Hz, *t*-Bu), 29.3 (q, $^1J_{CH}$ = 122.6 Hz, Me), 26.3 (t, $^1J_{CH}$ = 132.9 Hz, $C_6$), 24.0 (q, $^1J_{CH}$ = 125.3 Hz, Me), 13.1 (q, $^1J_{CH}$ = 129.2 Hz, $Cp'^{t}$ Me); $^1H$-$^{13}C$ HETCORR (100 MHz, $CDCl_3$) $\delta$ 129.7 ($C_{Ph}$) ↔ $\delta$ 7.79 ($H_{Ph}$); $\delta$ 129.3 ($C_{Ph}$) ↔ $\delta$ 7.50[a] ($H_{Ph}$); $\delta$ 95.4 ($C_2$) ↔ $\delta$ 5.52 ($H_2$); $\delta$ 88.8 ($Cp'^{t}$) ↔ $\delta$ 5.39 ($Cp'^{t}$); $\delta$ 86.0 ($Cp'^{t}$) ↔ $\delta$ 4.78 ($Cp'^{t}$); $\delta$ 85.3 ($Cp'^{t}$) ↔ $\delta$ 4.36 ($Cp'^{t}$); $\delta$ 80.2 ($C_5$) ↔ $\delta$ 5.10 ($H_5$);$\delta$ 44.5 ($C_7$) ↔ $\delta$ 2.65 ($H_{7endo}$), $\delta$ 1.85 ($H_{7exo}$); $\delta$ 30.3 (*t*-Bu) ↔ $\delta$ 1.42 (*t*-Bu); $\delta$ 29.3 (Me) ↔ $\delta$ 1.84 (Me); $\delta$ 26.3 ($C_6$) ↔ $\delta$ 1.97 ($H_{6endo}$), $\delta$ 0.61 ($H_{6exo}$); $\delta$ 24.0 (Me) ↔ $\delta$ 2.16 (Me); $\delta$ 13.1 ($Cp'^{t}$ Me) ↔ $\delta$ 2.20 ($Cp'^{t}$ Me). [a] Correlation is broad enough to encompass both $\delta$ 7.54 ($H_{Ph}$) and $\delta$ 7.47

($H_{Ph}$). Analysis calculated for $C_{25}H_{32}BCoF_4$: C, 62.78; H, 6.74; found: C, 62.499; H, 6.760.



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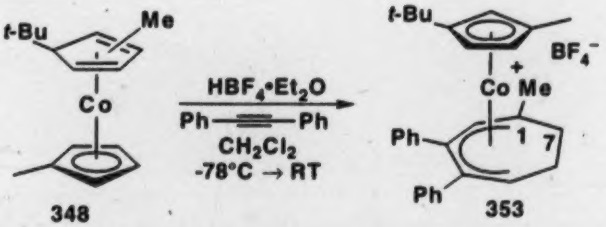
**[(*t*-Bu-Me-$C_5H_3$)Co(1,3,4-$Me_3C_7H_6$)]$^+$ $BF_4^-$ (352).** In the drybox, a flask was charged with Cp'Co(Cp'$^t$H) (**348**) (0.0649 g, 0.237 mmol) and removed to the Schlenk line, where dichloromethane (6 mL) was added. The solution was cooled to -78 °C and 2-butyne (0.20 mL, 10 equiv) was added. Upon addition of $HBF_4 \cdot Et_2O$ (38 µL, 1.1 equiv), the color deepened. After 2 h at -78 °C, the solution had turned a deep red color. Allowing the solution to warm to room temperature did not result in any further color change. Removal of all volatile material gave a dark red residue. The compound was purified by flash chromatography (silica gel) using 5% methanol-dichloromethane. After a red band was collected and the solvent was removed, there remained a red residue (0.074 g, 78%). This material was shown by $^1H$ NMR spectroscopy to contain a single major product, although minor impurities are present. IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3103 (w), 2969 (m), 1694 (w), 1483 (m), 1460 (m), 1382 (m), 1282 (w), 1222 (m), 1194 (w), 1058 (s), 864 (m), 818 (w), 733 (m), 701 (w), 520 (m); $^1H$ NMR (360 MHz, $CDCl_3$) $\delta$ 5.40-5.35 (narrow m, 2H, Cp'$^t$), 5.34 (s, 1H, $H_2$), 4.96 (dd, $J_{5\text{-}6endo}$ = 7.3 Hz, $J_{5\text{-}6exo}$ = 4.1 Hz, 1H, $H_5$), 4.60 (t, $J$ = 2.3 Hz, 1H, Cp'$^t$), 2.50 (s, 3H, $Me_3$), 2.39 (ddd, $J_{7endo\text{-}7exo}$ = 16.2 Hz, $J_{7endo\text{-}6endo}$ = 10 Hz, $J_{7endo\text{-}6exo}$ = 8 Hz, 1H, $H_{7endo}$), 2.15 (s, 3H, $Me_4$), 2.12 (m, dddd by decoupling, $J_{6endo\text{-}6exo}$ = 15 Hz, $J_{6endo\text{-}7endo}$ = 9 Hz, $J_{6endo\text{-}5}$ = 7.3 Hz, $J_{6endo\text{-}7exo}$ = 4 Hz, 1H, $H_{6endo}$), 1.87 (s, 3H, Cp'$^t$ Me), 1.81 (s, 3H, $Me_1$), 1.44 (ddd, $J_{7exo\text{-}7endo}$ = 15.9 Hz, $J_{7exo\text{-}6exo}$ = 6 Hz, $J_{7exo\text{-}6endo}$ = 5 Hz, 1H, $H_{7exo}$), 1.24 (s, 9H, *t*-Bu), 0.70 (m, dddd by decoupling, $J_{6exo\text{-}6endo}$ = 14.1 Hz, $J_{6exo\text{-}7endo}$ = 8 Hz, $J_{6exo\text{-}7exo}$ = 7 Hz, $J_{6exo\text{-}5}$ = 4.2

Hz, 1H, $H_{6exo}$); $^{1}H$-$^{1}H$ GCOSY (300 MHz, $CDCl_3$) δ 5.37 (Cp$'^{t}$) ↔ δ 4.60 (Cp$'^{t}$); δ 5.34 ($H_2$) ↔ δ 2.50 (w, $Me_3$), δ 2.15 (w, $Me_4$), δ 1.81 (w, $Me_1$), δ 1.44 (w, $J_{7exo}$); δ 4.96 ($H_5$) ↔ δ 2.12 ($H_{6endo}$), δ 0.70 ($H_{6exo}$); δ 4.60 (Cp$'^{t}$) ↔ δ 1.87 (w, Cp$'^{t}$ Me); δ 2.39 ($H_{7endo}$) ↔ δ 2.12 ($H_{6endo}$), δ 1.44 ($H_{7exo}$), δ 0.70 ($H_{6exo}$); δ 2.12 ($H_{6endo}$) ↔ δ 1.44 ($H_{7exo}$), δ 0.70 ($H_{6exo}$); δ 1.44 ($H_{7exo}$) ↔ δ 0.70 ($H_{6exo}$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 116.8 (s, Cp$'^{t}$ *t*-Bu ring quaternary), 111.7 (s, $C_3$), 109.5 (s, $C_1$), 107.0 (s, $C_4$), 97.2 (s, Cp$'^{t}$ Me ring quaternary), 93.7 (d, $^{1}J_{CH}$ = 161.4 Hz, $C_2$), 90.1 (d, $^{1}J_{CH}$ = 178.4 Hz, Cp$'^{t}$), 85.9 (d, $^{1}J_{CH}$ = 183.7 Hz, Cp$'^{t}$), 85.6 (d, $^{1}J_{CH}$ = 177.9 Hz, Cp$'^{t}$), 79.4 (d, $^{1}J_{CH}$ = 150.4 Hz, $C_5$), 41.4 (t, $^{1}J_{CH}$ = 129.2 Hz, $C_7$), 32.0 (s, *t*-Bu quaternary), 30.2[a] (q, $^{1}J_{CH}$ = 126.5 Hz, *t*-Bu and $Me_1$), 29.3 (t, $^{1}J_{CH}$ = 130.9 Hz, $C_6$), 21.3 (q, $^{1}J_{CH}$ = 128.8 Hz, $Me_4$), 21.1 (q, $^{1}J_{CH}$ = 129.3 Hz, $Me_3$), 12.4 (q, $^{1}J_{CH}$ = 129.2 Hz, Cp$'^{t}$ Me). [a] 2 carbon signals overlap: *t*-Bu and $Me_1$. HMQC (300 MHz, $CDCl_3$) δ 93.7 ($C_2$) ↔ δ 5.34 ($H_2$); δ 90.1 (Cp$'^{t}$) ↔ δ 5.37 (Cp$'^{t}$); δ 85.9 (Cp$'^{t}$) ↔ δ 5.37 (Cp$'^{t}$); δ 85.6 (Cp$'^{t}$) ↔ δ 4.60 (Cp$'^{t}$); δ 79.4 ($C_5$) ↔ δ 4.96 ($H_5$); δ 41.4 ($C_7$) ↔ δ 2.39 ($H_{7exo}$), δ 1.40 ($H_{7endo}$); δ 30.2 ($Me_1$ and *t*-Bu) ↔ δ 1.81 ($Me_1$), δ 1.24 (*t*-Bu); δ 29.3 ($C_6$) ↔ δ 2.12 ($H_{6endo}$), δ 0.70 ($H_{6exo}$); δ 21.3 ($Me_4$) ↔ δ 2.15 ($Me_4$); δ 21.1 ($Me_3$) ↔ δ 2.50 ($Me_3$); δ 12.4 (Cp$'^{t}$ Me) ↔ δ 2.87 (Cp$'^{t}$ Me); HMBC (300 MHz, $CDCl_3$) δ 116.8 (Cp$'^{t}$ *t*-Bu ring quaternary) ↔ δ 5.37 (Cp$'^{t}$), 4.60 (Cp$'^{t}$), 1.87 (Cp$'^{t}$ Me), 1.24 (*t*-Bu); δ 111.7 ($C_3$) ↔ δ 4.96 ($H_5$), δ 2.50 ($Me_3$), δ 2.15 ($Me_4$); δ 109.5 ($C_1$) ↔ δ 1.81 ($Me_1$), δ 0.70 ($H_{6exo}$); δ 107.0 ($C_4$) ↔ δ 5.34 ($H_2$), δ 4.96 (w, $H_5$), δ 2.50 ($Me_3$), δ 2.15 ($Me_4$), δ 0.70 ($H_{6exo}$); δ 97.2 (Cp$'^{t}$ Me ring quaternary) ↔ δ 5.37 (Cp$'^{t}$), 4.60 (Cp$'^{t}$), 1.87 (Cp$'^{t}$ Me); δ 93.7 ($C_2$) ↔ δ 2.50 ($Me_3$), δ 2.39 ($H_{7endo}$), δ 1.81 ($Me_1$); δ 90.1 (Cp$'^{t}$) ↔ δ 5.37 (Cp$'^{t}$), 4.60 (Cp$'^{t}$), 1.87 (Cp$'^{t}$ Me); δ 85.9/85.6[a] (Cp$'^{t}$) ↔ δ 5.37 (Cp$'^{t}$), 4.60 (Cp$'^{t}$); δ 79.4 ($C_5$) ↔ δ 2.39 ($H_{7endo}$), δ 2.15 ($Me_4$); δ 41.4 ($C_7$) ↔ δ 5.34 ($H_2$), δ 4.96 ($H_5$), δ 1.81 ($Me_1$), δ 0.70 ($H_{6exo}$); δ 30.2 ($Me_1$ and *t*-Bu) ↔ δ 5.34 ($H_2$), δ 1.24 (*t*-Bu); δ 29.3 ($C_6$) ↔ δ 4.96 ($H_5$), δ 2.39 ($H_{7endo}$); δ 21.3 ($Me_4$) ↔ δ 4.96 ($H_5$); δ 21.1 ($Me_3$) ↔ δ 5.34 ($H_2$). [a] Resolution is insufficient to assign signals.

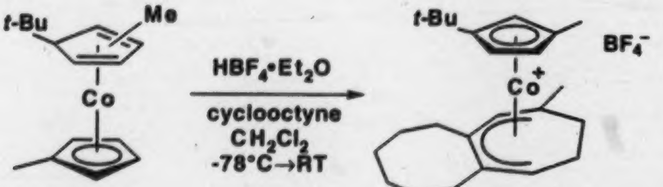
Electrospray MS *m/z* calculated for $C_{20}H_{30}Co$ ($M^+$-$BF_4$): 329.167949; found: 329.168582 (100%).



**348** **353**

**[(*t*-Bu-Me-$C_5H_3$)Co(1-Me-3,4-$Ph_2C_7H_6$)]$^+$ $BF_4^-$ (353).** In the drybox, a flask was charged with Cp'Co(Cp'$^t$H) (**348**) (0.1058 g, 0.3857 mmol) and removed to the Schlenk line, where dichloromethane (11 mL) was added. The solution was cooled to -78 °C and diphenylacetylene (0.344 g, 5 equiv) was added. Upon addition of $HBF_4•Et_2O$ ( 0.063 mL, 1.1 equiv), the color turned to green. Allowing the solution to warm to room temperature over several hours resulted in a color change to deep red. Removal of all volatile material gave a dark oily residue. The compound was purified by flash chromatography (silica gel) using 5% methanol-dichloromethane. After a red band was collected and the solvent was removed, there remained a red residue (0.1610 g, 77%). This material was shown by $^1H$ NMR spectroscopy to contain a single major product, although minor impurities are present. Recrystallization from chloroform/diethyl ether yielded an orange powder (0.1201 g, 58%), which contained predominantly one isomer. IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3060 (m), 2966 (m), 1695 (w), 1652 (w), 1599 (w), 1483 (m), 1445 (m), 1420 (m), 1367 (m), 1270 (m), 1221 (w), 1184 (w), 1057 (s), 855 (w), 765 (m), 733 (m), 703 (s), 625 (w), 596 (w), 557 (m), 535 (w), 520 (m); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.60 (br s, 2H, $H_{Ph}$), 7.40-7.00 (series of m, 8H, $H_{Ph}$), 5.68 (s, 1H, $H_2$), 5.41 (dd, $J$ = 8.1, 4.5 Hz, 1H, $H_5$), 5.37 (br s, 1H, Cp'$^t$), 5.09 (br s, 1H, Cp'$^t$), 3.47 (br s, 1H, Cp'$^t$), 2.84 (ddd, $J$ = 18.3, 9.6, 9.6 Hz, 1H, $H_{7endo}$), 2.34 (s, 3H, Cp'$^t$ Me), 2.20-2.00 (m, 2H, $H_{6endo}$ and $H_{7exo}$), 1.92 (s, 3H, $Me_1$), 1.16 (s, 9H, *t*-Bu), 0.65-0.50 (m, 1H, $H_{6exo}$); $^1H$-$^1H$ GCOSY (300 MHz, $CDCl_3$) $\delta$ 7.60 ($H_{Ph}$) ↔ $\delta$ 7.40 ($H_{Ph}$); $\delta$ 5.68 ($H_2$) ↔ $\delta$ 2.10

(H$_{7exo/6endo}$); $\delta$ 5.41 (H$_2$) $\leftrightarrow$ $\delta$ 2.10 (H$_{7exo/6endo}$), $\delta$ 0.57 (H$_{6exo}$); $\delta$ 5.37 (Cp$'^{t}$) $\leftrightarrow$ $\delta$ 5.09 (Cp$'^{t}$), $\delta$ 3.47 (Cp$'^{t}$), $\delta$ 2.34 (w, Cp$'^{t}$ Me); $\delta$ 5.09 (Cp$'^{t}$) $\leftrightarrow$ $\delta$ 3.47 (Cp$'^{t}$); $\delta$ 3.47 (Cp$'^{t}$) $\leftrightarrow$ $\delta$ 2.34 (w, Cp$'^{t}$ Me); $\delta$ 2.84 (H$_{7endo}$) $\leftrightarrow$ $\delta$ 2.10 (H$_{7exo/6endo}$), $\delta$ 0.57 (H$_{6exo}$); $\delta$ 2.10 (H$_{7exo/6endo}$) $\leftrightarrow$ $\delta$ 0.57 (H$_{6exo}$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.3 (s, C$_{Ph}$), 136.1 (s, C$_{Ph}$), 131.4 (d, $^1J_{CH}$ = 159.6 Hz, C$_{Ph}$), 130.4 (d, $^1J_{CH}$ = 160.1 Hz, C$_{Ph}$), 130.0 (d, $^1J_{CH}$ = 162.6 Hz, C$_{Ph}$), 129.46$^a$ (d, $^1J_{CH}$ = 160.4 Hz, C$_{Ph}$), 129.38$^a$ (d, $^1J_{CH}$ = 160.4 Hz, C$_{Ph}$), 128.2 (d, $^1J_{CH}$ = 162.9 Hz, C$_{Ph}$), 117.3 (s, C quaternary), 114.3 (s, C quaternary), 110.2 (s, C quaternary), 109.1 (s, C quaternary), 98.5 (s, C quaternary), 95.8 (d, $^1J_{CH}$ = 164.5 Hz, C$_2$), 91.1 (d, $^1J_{CH}$ = 180.3 Hz, C$_5$), 89.2 (d, $^1J_{CH}$ = 170.5 Hz, Cp$^{t}$), 85.8 (d, $^1J_{CH}$ = 182.6 Hz, Cp$^{t}$), 76.1$^b$ (d, Cp$'^{t}$), 46.2 (t, $^1J_{CH}$ = 132.0 Hz, C$_7$), 32.1 (s, *t*-Bu quaternary), 29.8 (q, $^1J_{CH}$ = 130.9 Hz, *t*-Bu), 29.1 (q, $^1J_{CH}$ = 123.0 Hz, Me$_1$), 25.1 (t, $^1J_{CH}$ = 129.3 Hz, C$_6$), 12.7 (q, $^1J_{CH}$ = 129.3 Hz, Cp$^{t}$ Me). $^a$ Signals overlap in gated spectrum. $^b$Signal obscured by solvent peak in the gated decoupled spectrum. HMQC (300 MHz, CDCl$_3$) $\delta$ 131.4-128.2 (C$_{Ph}$) $\leftrightarrow$ $\delta$ 7.6-7.0 (H$_{Ph}$); $\delta$ 95.8 (C$_2$) $\leftrightarrow$ $\delta$ 5.68 (H$_2$); $\delta$ 91.1 (C$_5$) $\leftrightarrow$ $\delta$ 5.41 (H$_5$); $\delta$ 89.2 (Cp$'^{t}$) $\leftrightarrow$ $\delta$ 3.47 (Cp$'^{t}$); $\delta$ 85.8 (Cp$^{t}$) $\leftrightarrow$ $\delta$ 5.09 (Cp$'^{t}$); $\delta$ 76.1 (Cp$'^{t}$) $\leftrightarrow$ $\delta$ 5.37 (Cp$'^{t}$); $\delta$ 46.2 (C$_7$) $\leftrightarrow$ $\delta$ 2.84 (H$_{7endo}$), $\delta$ 2.10 (H$_{7exo}$); $\delta$ 29.8 (*t*-Bu) $\leftrightarrow$ $\delta$ 1.16 (*t*-Bu); $\delta$ 29.1 (Me$_1$) $\leftrightarrow$ $\delta$ 1.92 (Me$_1$); $\delta$ 25.1 (C$_6$) $\leftrightarrow$ $\delta$ 2.00 (H$_{6endo}$), $\delta$ 0.57 (H$_{6exo}$); $\delta$ 12.7 (Cp$'^{t}$ Me) $\leftrightarrow$ $\delta$ 2.34 (Cp$'^{t}$ Me). Analysis calculated for $C_{30}H_{34}BCoF_4$: C, 66.70; H, 6.34; found: C, 67.739; H, 6.532. Electrospray MS *m/z* calculated for $C_{30}H_{34}Co$ (M$^+$-BF$_4$): 453.199249; found: 453.199905 (100%).



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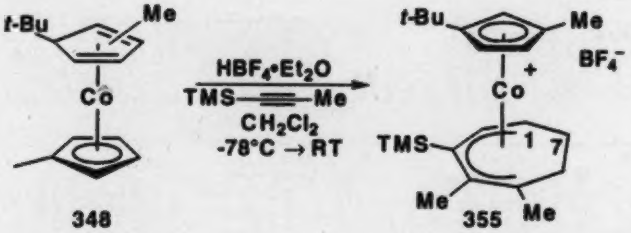
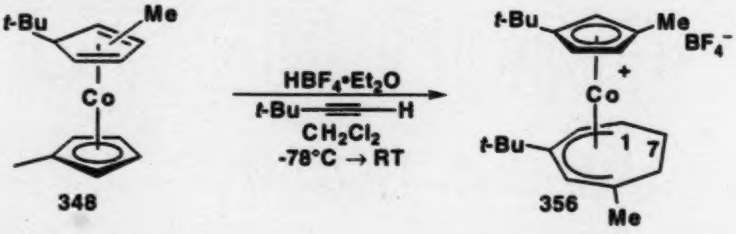
**[(*t*-Bu-Me-C$_5$H$_3$)Co(1-MeC$_{13}$H$_{18}$)]$^+$ BF$_4^-$ (354).** In the drybox, a flask was charged with Cp'Co(Cp$''^{t}$H) (**348**) (0.1574 g, 0.5738 mmol) and removed to the Schlenk line, where dichloromethane (15 mL) was added. The solution was cooled to -78 °C and $HBF_4{\bullet}Et_2O$ (0.110 mL, 1.3 equiv) was added, turning the solution from red-orange to deep green. Cyclooctyne (0.16 mL, 2 equiv) was then added, causing the solution to change to a deep red color. Warming slowly to room temperature did not cause any further color change. Removal of all volatile material gave a deep red residue. The compound was purified by flash chromatography (silica gel) using 5% methanol-dichloromethane. After a red band was collected and the solvent was removed, there remained a red residue. As recrystallization attempts returned only oils, this compound was subjected to further chromatography, giving a red solid (0.1150 g, 43%), which proved to be predominantly one isomer. IR ($CDCl_3$ cast, $cm^{-1}$) 3105 (w), 2926 (s), 2857 (s), 2261(w), 1712 (w), 1482 (m), 1455 (s), 1381(m), 1363 (m), 1281 (m), 1222 (m), 1168 (w), 1058 (s), 916 (m), 866 (m), 729 (s), 647 (w), 520 (m); $^1H$ NMR (360 MHz, $CDCl_3$) $\delta$ 5.50 (t, $J$ = 2.7 Hz, 1H, $Cp'^{t}$), 5.41 (t, $J$ = 2.2 Hz, 1H, $Cp'^{t}$), 5.14 (s, 1H, $H_2$), 4.92 (dd, $J_{5\text{-}6endo}$ = 7.7 Hz, $J_{5\text{-}6exo}$ = 4.3 Hz, 1H, $H_5$), 4.58 (t, $J$= 2.3 Hz, $Cp'^{t}$), 3.27 (td, $J$ = 13.0, 4.3 Hz, 1H, $CH_2$), 2.95-2.80 (m, 2H, $CH_2$), 2.62 (dt, $J_{7endo\text{-}7exo}$ = 16.7 Hz, $J_{7endo\text{-}6exo} = J_{7endo\text{-}6endo}$ = 9.1 Hz, 1H, $H_{7endo}$), 2.2-1.2 (series of m, $CH_2$, $H_{6endo}$ and $H_{7exo}$), 1.87 (s, 3H, Me), 1.85 (s, 3H, Me), 1.27 (s, 9H, *t*-Bu), 0.46 (m, dddd by decoupling, $J_{6exo\text{-}6endo}$ = 14.3 Hz, $J_{6exo\text{-}7endo}$ = 8.9 Hz, $J_{6exo\text{-}7exo}$ = 5.6 Hz, $J_{6exo\text{-}5}$ = 4.3 Hz, 1H, $H_{6exo}$); $^1H$-$^1H$ GCOSY (300 MHz, $CDCl_3$) $\delta$ 5.50 ($Cp'^{t}$) ↔ $\delta$ 5.41 ($Cp'^{t}$), $\delta$ 4.58 ($Cp'^{t}$); $\delta$ 5.41 ($Cp'^{t}$) ↔ $\delta$ 4.58 ($Cp'^{t}$); $\delta$ 5.14 ($H_2$) ↔ $\delta$ 1.63 ($H_{6endo}$); $\delta$ 4.92 ($H_5$) ↔ $\delta$ 2.05 ($H_{7exo}$), $\delta$ 0.46 ($H_{6exo}$); $\delta$ 3.27 ($CH_2$) ↔ $\delta$ 2.95 ($CH_2$), $\delta$ 2.10 (w, $CH_2$), $\delta$ 1.67 (w, $CH_2$); $\delta$ 2.95 ($CH_2$) ↔ $\delta$ 1.90 (w, $CH_2$), $\delta$ 1.67 (w, $CH_2$); $\delta$ 2.62 ($H_{7endo}$) ↔ $\delta$ 2.05 ($H_{7exo}$), $\delta$ 1.63 ($H_{6endo}$), $\delta$ 0.46 ($H_{6exo}$); $\delta$ 2.05 ($H_{7exo}$) ↔ $\delta$ 1.63 ($H_{6endo}$), $\delta$ 0.46 ($H_{6exo}$); $\delta$ 1.63 ($H_{6endo}$) ↔ $\delta$ 0.46 ($H_{6exo}$). Several unassigned correlations appear within the region of $\delta$ 2.2-1.2. $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 117.2 (s, quaternary), 114.5 (s, quaternary), 110.8 (s, quaternary), 110.6 (s, quaternary), 97.7 (s, quaternary), 92.9 (d, $^1J_{CH}$ = 159.0 Hz, $C_2$), 90.3 (d, $^1J_{CH}$ = 183.4 Hz, $Cp^{t}$), 85.5$^a$ (d, $^1J_{CH}$ = 184 Hz, $Cp^{t}$), 85.3$^a$ (d, $^1J_{CH}$ = 178 Hz, $Cp^{t}$), 78.4 (d, $^1J_{CH}$ = 147 Hz, $C_5$), 43.3 (t, $^1J_{CH}$ = 129.1 Hz, $C_7$), 35.5 (t,

$^1J_{CH}$ = 135.3 Hz, CH$_2$), 33.7 (t, $^1J_{CH}$ = 134.9 Hz, CH$_2$), 32.0$^b$ (t, CH$_2$), 31.0$^b$ (t, CH$_2$), 30.4 (q, $^1J_{CH}$ = 127.1 Hz, *t*-Bu), 30.1 (q, $^1J_{CH} \approx$ 127 Hz, Me), 28.3 (t, $^1J_{CH}$ = 130.7 Hz, C$_6$), 26.4 (t, $^1J_{CH} \approx$ 121 Hz, CH$_2$), 25.6 (t, $^1J_{CH}$ = 124.4 Hz, CH$_2$), 12.8 (q, $^1J_{CH}$ = 129.3 Hz, Cp'$^t$ Me). $^a$ Signals overlap, *J*'s are approximated. $^b$ Signal obscured in gated decoupled spectrum. No $^1J_{CH}$ value obtained. $^1$H-$^{13}$C HETCORR (100 MHz, CDCl$_3$) δ 92.9 (C$_2$) ↔ δ 5.14 (H$_2$); δ 90.3 (Cp'$^t$) ↔ δ 5.41 (Cp'$^t$); δ 85.5 (Cp'$^t$) ↔ δ 5.50 (Cp'$^t$); δ 85.3 (Cp'$^t$) ↔ δ 4.58 (Cp'$^t$); δ 78.4 (C$_5$) ↔ δ 4.92 (H$_5$); δ 43.3 (C$_7$) ↔ δ 2.62 (H$_{7endo}$), δ 1.63 (H$_{7exo}$); δ 35.5 (CH$_2$) ↔ δ 2.80 (CH$_2$), δ 1.95 (CH$_2$); δ 33.7 (CH$_2$) ↔ δ 3.27 (CH$_2$), δ 2.90 (CH$_2$); δ 32.0 (CH$_2$) ↔ δ 2.15 (CH$_2$), δ 1.50 (CH$_2$); δ 31.0 (CH$_2$) ↔ δ 2.10 (CH$_2$), δ 1.70 (CH$_2$); δ 30.4 (*t*-Bu) ↔ δ 1.27 (*t*-Bu); δ 30.1 (Me) ↔ δ 1.85 (Me); δ 26.4 (CH$_2$) ↔ δ 1.70 (CH$_2$), δ 1.50 (CH$_2$); δ 25.6 (CH$_2$) ↔ δ 1.75 (CH$_2$), δ 1.40 (CH$_2$); δ 12.8 (Cp'$^t$ Me) ↔ δ 1.87 (Cp'$^t$ Me). Electrospray MS *m/z* calculated for C$_{24}$H$_{36}$Co (M$^+$-BF$_4$): 383.214899; found: 383.215271. (100 %).



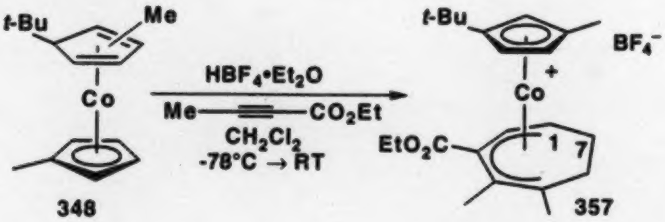
**[(*t*-Bu-Me-C$_5$H$_3$)Co(4,5-Me$_2$-3-(SiMe$_3$)C$_7$H$_6$)]$^+$ BF$_4^-$ (355).** In the drybox, a flask was charged with Cp'Co(Cp'$^t$H) (**248**) (0.1872 g, 0.6824 mmol) and removed to the Schlenk line, where dichloromethane (18 mL) was added. The solution was cooled to -78 °C and 1-(trimethylsilyl)propyne (0.31 mL, 3 equiv) was added. Upon addition of HBF$_4$•Et$_2$O (0.221 mL, 2.2 equiv), the color turned to green. Allowing the solution to warm to room temperature over several hours resulted in a color change to deep red. Removal of all volatile material gave a dark oily residue. The compound was purified by flash chromatography (silica gel) using 5% methanol-dichloromethane. After a red band was collected and the solvent was removed, there remained a red residue. In another experiment, this residue, although obtained in high yield (84%), appeared to contain multiple species. The red solid was recrystallized from dichloromethane/diethyl ether to give a single dark red isomer (0.1401 g, 43%). The $^1$H NMR spectrum of the mother liquor indicated the presence of several unisolable compounds. IR ($CDCl_3$ cast, cm$^{-1}$) 3105 (w), 2960 (s), 2835 (m), 2166 (w), 1624 (w), 1482 (m), 1436 (m), 1381 (m), 1363 (m), 1336 (m), 1305 (m), 1255 (s), 1219 (m), 1058 (s), 958 (m), 923 (m), 843 (s), 797 (w), 764 (m), 727 (m), 693 (w), 639 (m), 533 (m), 522 (m), 278 (w), 449 (w); $^1$H NMR (300 MHz, $CDCl_3$) δ 5.31 (t, $J$ = 2.1 Hz, 1H, Cp$'^{t}$), 5.00 (t, $J$ = 2.7 Hz, 1H, Cp$'^{t}$), 4.97 (d, $J_{2\text{-}1}$ = 9.3 Hz, 1H, $H_2$), 4.88 (dq, $J_{1\text{-}2}$ = 9.3 Hz, $J_{1\text{-}7\mathrm{endo}} = J_{1\text{-}7\mathrm{exo}} = J_{1\text{-}6\mathrm{endo}} \approx$ 2.7 Hz, 1H, $H_1$), 4.68 (dd, $J$ = 2.7, 2.1 Hz, 1H, Cp$'^{t}$), 3.14 (dddd, $J_{7\mathrm{endo}\text{-}7\mathrm{exo}}$ = 17.7 Hz, $J_{7\mathrm{endo}\text{-}6\mathrm{exo}}$ = 12.7 Hz, $J_{7\mathrm{endo}\text{-}6\mathrm{endo}}$ = 6.9 Hz, $J_{7\mathrm{endo}\text{-}1}$ = 2.7 Hz, 1H, $H_{7\mathrm{endo}}$), 2.54 (s, 3H, $Me_4$), 2.47 (s, 3H, Cp$'^{t}$ Me), 2.31 (ddd, $J_{7\mathrm{exo}\text{-}7\mathrm{endo}}$ = 16.8 Hz, $J_{7\mathrm{exo}\text{-}6\mathrm{exo}}$ = 4.6 Hz, $J_{7\mathrm{exo}\text{-}1} \approx$ 2.7 Hz, 1H, $H_{7\mathrm{exo}}$), 1.79 (s, 3H, $Me_5$), 1.21 (ddd, $J_{6\mathrm{endo}\text{-}6\mathrm{exo}}$ = 11.4 Hz, $J_{6\mathrm{endo}\text{-}7\mathrm{endo}}$ = 6.6 Hz, $J_{6\mathrm{endo}\text{-}1}$ = 1.8 Hz, 1H, $H_{6\mathrm{endo}}$), 1.12 (s, 9H, *t*-Bu), 0.55 (s, 9H, $SiMe_3$), 0.03 (ddd, $J_{6\mathrm{exo}\text{-}7\mathrm{endo}}$ = 12.6 Hz, $J_{6\mathrm{exo}\text{-}6\mathrm{endo}}$ = 11.7 Hz, $J_{6\mathrm{exo}\text{-}7\mathrm{exo}}$ = 5.1 Hz, 1H, $H_{6\mathrm{exo}}$); $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) δ 5.31 (Cp$'^{t}$) ↔ δ 5.00 (Cp$'^{t}$), δ 4.68 (Cp$'^{t}$), δ 2.47 (w, Cp$'^{t}$ Me); δ 5.00 (Cp$'^{t}$) ↔ δ 4.68 (Cp$'^{t}$); δ 4.97 ($H_2$) ↔ δ 4.88 ($H_1$), δ 2.54 (w, $Me_4$), δ 2.31 (w, $H_{7\mathrm{exo}}$); δ 4.88 ($H_1$) ↔ δ 3.14 ($H_{7\mathrm{endo}}$), δ 2.31 ($H_{7\mathrm{exo}}$), δ 1.21 (w, $H_{6\mathrm{endo}}$); δ 3.14 ($H_{7\mathrm{endo}}$) ↔ δ 2.31 ($H_{7\mathrm{exo}}$), δ 1.21 ($H_{6\mathrm{endo}}$), δ 0.03 ($H_{6\mathrm{exo}}$); δ 2.31[a] ($H_{7\mathrm{endo}}$) ↔ δ 0.03 ($H_{6\mathrm{exo}}$); δ 1.21 ($H_{6\mathrm{endo}}$) ↔ δ 0.03 ($H_{6\mathrm{exo}}$); [a]No cross peak to δ 1.21 ($H_{6\mathrm{endo}}$) is observed. $^{13}$C NMR[a] (100 MHz, $CDCl_3$) δ 115.3 (s, $C_5$), 114.5 (s, $C_3$), 112.7 (s, Cp$'^{t}$ *t*-Bu ring quaternary), 105.2 (s, s, Cp$'^{t}$ Me ring quaternary), 99.0 (s, $C_4$), 93.7 (d, $^1J_{CH}$ = 164 Hz, $C_2$), 93.2 (d, $^1J_{CH}$ = 185 Hz, Cp$'^{t}$), 92.1 (d, $^1J_{CH}$ = 154 Hz, $C_1$), 86.1 (d, $^1J_{CH}$ = 180 Hz, Cp$'^{t}$), 81.9 (d, $^1J_{CH}$ = 181 Hz, Cp$'^{t}$), 41.9 (t, $^1J_{CH}$ = 126 Hz, $C_7$), 34.1 (t, $^1J_{CH}$ = 130 Hz, $C_6$), 32.3 (q, $^1J_{CH}$ = 127 Hz, $Me_5$), 29.9 (q, $^1J_{CH}$ = 126 Hz, *t*-Bu), 24.3 (q, $^1J_{CH}$ = 129 Hz, $Me_4$), 14.9 (q, $^1J_{CH}$ = 132 Hz, Cp$'^{t}$ Me), 2.9 (q, $^1J_{CH}$ = 122 Hz, $SiMe_3$). [a] $^1J_{CH}$ values are obtained from the HMQC spectrum. HMQC (300 MHz, $CDCl_3$) δ 93.7 ($C_2$) ↔ δ 4.97 ($H_2$); δ

93.2 ($Cp'^{t}$) ↔ δ 5.31 ($Cp'^{t}$); δ 92.1 ($C_1$) ↔ δ 4.88 ($H_1$); δ 86.1 ($Cp'^{t}$) ↔ δ 4.68 ($Cp'^{t}$); δ 81.9 ($Cp'^{t}$) ↔ δ 5.00 ($Cp'^{t}$); δ 41.9 ($C_7$) ↔ δ 3.14 ($H_{7endo}$), δ 2.31 ($H_{7exo}$); δ 34.1 ($C_6$) ↔ δ 1.20 ($H_{6endo}$), δ 0.03 ($H_{6exo}$); δ 32.3 ($Me_5$) ↔ δ 1.79 ($Me_5$); δ 29.9 (*t*-Bu) ↔ δ 1.12 (*t*-Bu); δ 24.3 ($Me_4$) ↔ δ 2.54 ($Me_4$); δ 14.9 ($Cp'^{t}$ Me) ↔ δ 2.47 ($Cp'^{t}$ Me); δ 2.9 ($SiMe_3$) ↔ δ 0.55 ($SiMe_3$); HMBC (300 MHz, $CDCl_3$) δ 115.3 ($C_5$) ↔ δ 1.79 ($Me_5$), δ 0.03 ($H_{6exo}$); δ 114.5 ($C_3$) ↔ δ 2.54 ($Me_4$), δ 4.88 ($H_1$); δ 112.7 ($Cp'^{t}$ quaternary) ↔ δ 5.31 ($Cp'^{t}$), δ 5.00 ($Cp'^{t}$), δ 4.68 ($Cp'^{t}$), δ 2.47 ($Cp'^{t}$ Me), δ 1.12 (*t*-Bu); δ 105.2 ($Cp'^{t}$ quaternary) ↔ δ 5.31 ($Cp'^{t}$), δ 5.00 ($Cp'^{t}$), δ 4.68 ($Cp'^{t}$), δ 2.47 ($Cp'^{t}$ Me); δ 99.0 ($C_4$) ↔ δ 4.97 ($H_2$), δ 2.54 ($Me_4$), δ 1.79 ($Me_5$), δ 0.03 ($H_{6exo}$); δ 93.7 ($C_2$)/ 93.2 ($Cp'^{t}$)/ 92.1 ($C_1$)$^{a}$ ↔ δ 5.31 ($Cp'^{t}$), δ 5.00 ($Cp'^{t}$), δ 4.68 ($Cp'^{t}$), δ 3.14 ($H_{7endo}$), δ 2.54 ($Me_4$), δ 2.47 ($Cp'^{t}$ Me); δ 86.1 ($Cp'^{t}$) ↔ δ 5.31 ($Cp'^{t}$), δ 5.00 ($Cp'^{t}$); δ 81.9 ($Cp'^{t}$) ↔ δ 5.31 ($Cp'^{t}$), δ 4.68 ($Cp'^{t}$); δ 41.9 ($C_7$) ↔ δ 4.97 ($H_2$), δ 4.88 ($H_1$), δ 0.03 ($H_{6exo}$); δ 34.1 ($C_6$) ↔ δ 3.14 ($H_{7endo}$), δ 1.79 ($Me_5$); δ 32.3 ($Me_5$) ↔ δ 0.03 ($H_{6exo}$); δ 29.9 (*t*-Bu) ↔ δ 1.12 (*t*-Bu); δ 24.3 ($Me_4$) ↔ δ 4.97 ($H_2$), δ 4.88 ($H_1$); δ 2.9 ($SiMe_3$) ↔ δ 0.55 ($SiMe_3$). $^{a}$Resolution is insufficient to assign correlations to individual carbon signals. Analysis calculated for $C_{22}H_{36}BCoF_4Si$: C, 55.71; H, 7.65; found: C, 55.547; H, 7.753.



**[(*t*-Bu-Me-$C_5H_3$)Co(3-*t*-Bu-1-Me$C_7H_7$)]$^{+}$ $BF_4^{-}$ (356).** In the drybox, a flask was charged with Cp'Co($Cp'^{t}$H) (**348**) (0.0808 g, 0.295 mmol) and removed to the Schlenk line, where dichloromethane (8 mL) was added. The solution was cooled to -78 °C and 3,3-dimethyl-1-butyne (0.36 mL, 10 equiv) was added. Upon addition of $HBF_4•Et_2O$ (48 µL, 1.1 equiv), the color turned to green. After 2 h at -78 °C, the solution had turned a deep red color. Allowing the solution to warm to room temperature did not result in any further color change. Removal of all volatile material gave a dark oily residue. The compound was purified by flash chromatography (silica gel) using 5% methanol-dichloromethane. After a red band was collected and the solvent was removed, there remained a red residue (0.1090 g, 83%). This material was shown by $^1$H NMR spectroscopy to contain a single major product, although minor impurities are present. IR ($CH_2Cl_2$ cast, cm$^{-1}$) 3105 (w), 2966 (s), 2875 (m), 1715 (w), 1683 (w), 1652 (w), 1615 (w), 1538 (w), 1482 (m), 1464 (m), 1398 (w), 1367 (m), 1282 (w), 1219 (m), 1059 (s), 861 (m), 819 (w), 764 (w), 733 (w), 696 (w), 520 (m); $^1$H NMR (360 MHz, $CDCl_3$) $\delta$ 5.68 (br s, 1H, $H_4$), 5.37 (t, $J = 2.0$ Hz, 1H, Cp$'^{t}$), 5.28 (d, $J_{2\text{-}1} = 8.5$ Hz, 1H, $C_2$), 4.99 (t, $J = 2.8$ Hz, 1H, Cp$'^{t}$), 4.80 (dd, $J = 2.8$, 1.8 Hz, 1H, Cp$'^{t}$), 4.64 (ddd, $J_{1\text{-}2} = 9.0$ Hz, $J_{1\text{-}7exo} = J_{1\text{-}7endo} = 4.1$ Hz, 1H, $H_1$), 2.85 (dddd, $J_{7endo\text{-}7exo} = 16.3$ Hz, $J_{7endo\text{-}6endo} = J_{7endo\text{-}6exo} = 8.8$ Hz, $J_{7endo\text{-}1} = 4.8$ Hz, 1H, $H_{7endo}$), 2.55 (s, 3H, Cp$'^{t}$ Me), 1.90 (m, dddd by decoupling, $J_{6endo\text{-}6exo} = 13.8$ Hz, $J_{6endo\text{-}7endo} = 8.8$ Hz, $J_{6endo\text{-}7exo} = 3.4$ Hz, $J_{6endo\text{-}1} < 2$Hz, 1H, $H_{6endo}$), 1.81 (s, 3H, $Me_5$), 1.65 (m, dddd by decoupling, $J_{7exo\text{-}7endo} = 16.0$ Hz, $J_{7exo\text{-}6exo} = 6.0$ Hz, $J_{7exo\text{-}6endo} = 3.4$ Hz, $J_{7exo\text{-}1} = 4.0$ Hz, 1H, $H_{7exo}$), 1.57 (s, 9H, $C_3$ *t*-Bu), 1.18 (s, 9H, Cp$'^{t}$ *t*-Bu), 0.73 (ddd, $J_{6exo\text{-}6endo} = 14.3$ Hz, $J_{6exo\text{-}7endo} = 9.4$ Hz, $J_{6exo\text{-}7exo} = 6.0$ Hz, 1H, $H_{6exo}$); $^1$H-$^1$H GCOSY (300 MHz, $CDCl_3$) $\delta$ 5.68 ($H_4$) $\leftrightarrow$ $\delta$ 5.28 (w, $H_2$); $\delta$ 5.37 (Cp$'^{t}$) $\leftrightarrow$ $\delta$ 4.99 (Cp$'^{t}$), $\delta$ 4.80 (Cp$'^{t}$), $\delta$ 2.55 (w, Cp$'^{t}$Me); $\delta$ 5.28 ($H_2$) $\leftrightarrow$ $\delta$ 4.64 ($H_1$), $\delta$ 1.65 ($H_{7exo}$); $\delta$ 4.99 (Cp$'^{t}$) $\leftrightarrow$ $\delta$ 4.80 (Cp$'^{t}$); $\delta$ 4.64 ($H_1$) $\leftrightarrow$ $\delta$ 2.85 ($H_{7endo}$), $\delta$ 1.65 ($H_{7exo}$); $\delta$ 2.85 ($H_{7endo}$) $\leftrightarrow$ $\delta$ 1.90 ($H_{6endo}$), $\delta$ 1.65 ($H_{7exo}$); $\delta$ 1.90 ($H_{6endo}$) $\leftrightarrow$ $\delta$ 1.65 ($H_{7exo}$), $\delta$ 0.73 ($H_{6exo}$); $\delta$ 1.65 ($H_{7exo}$) $\leftrightarrow$ $\delta$ 0.73 ($H_{6exo}$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 127.2 (s, $C_3$), 113.7 (s, $C_5$), 112.5 (s, Cp$'^{t}$ *t*-Bu ring quaternary), 102.3 (s, Cp$'^{t}$ Me ring quaternary), 93.2 (d, $^1J_{CH} = 175.7$ Hz, Cp$'^{t}$), 88.0$^a$ (d, $^1J_{CH} = 165.4$ Hz, $C_2$), 87.9$^a$ (d, $^1J_{CH} = 165.4$ Hz, $C_4$), 84.9 (d, $^1J_{CH} = 179.5$ Hz, Cp$'^{t}$), 83.5 (d, $^1J_{CH} = 152.7$ Hz, $C_1$), 81.0 (d, $^1J_{CH} = 182.5$ Hz, Cp$'^{t}$), 37.7 (t, $^1J_{CH} = 125.8$ Hz, $C_7$), 35.8 (s, $C_3$ *t*-Bu quaternary), 35.3 (t, $^1J_{CH} = 125$ Hz, $C_6$), 32.4 (s, Cp$'^{t}$ *t*-Bu quaternary), 31.4 (q, $^1J_{CH} = 127.3$ Hz, $C_3$ *t*-Bu), 30.3 (q, $^1J_{CH} = 127^b$ Hz, $Me_5$), 29.8 (q, $^1J_{CH} = 126.0$

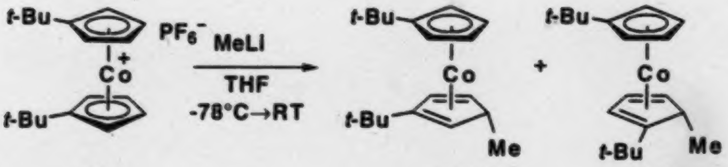
Hz, $Cp'^{t}$ *t*-Bu), 14.7 (q, $^{1}J_{CH}$ = 128.8 Hz, $Cp'^{t}$Me). [a]Carbons overlap in gated decoupled spectrum. [b]*J* value obtained from HMQC spectrum. HMQC (300 MHz, $CDCl_3$) δ 93.2 ($Cp'^{t}$) ↔ δ 5.37 ($Cp'^{t}$); δ 88.0 ($C_2$) ↔ δ 5.28 ($H_2$); δ 87.9 ($C_4$) ↔ δ 5.68 ($H_4$); δ 84.9 ($Cp'^{t}$) ↔ δ 4.80 ($Cp'^{t}$); δ 83.5 ($C_1$) ↔ δ 4.64 ($H_1$); δ 81.0 ($Cp'^{t}$) ↔ δ 4.99 ($Cp'^{t}$); δ 37.7 ($C_7$) ↔ δ 2.85 ($H_{7endo}$), δ 1.65 ($H_{7exo}$); δ 35.3 ($C_6$) ↔ δ 1.90 ($H_{6endo}$), δ 0.73 ($H_{6exo}$); δ 31.4 ($C_3$ *t*-Bu) ↔ δ 1.57 ($C_3$ *t*-Bu); δ 30.3 ($Me_5$) ↔ δ 1.81 ($Me_5$); δ 29.8 ($Cp'^{t}$ *t*-Bu) ↔ δ 1.18 ($Cp'^{t}$ *t*-Bu); δ 14.7 ($Cp'^{t}$ Me) ↔ δ 2.55 ($Cp'^{t}$ Me); HMBC (300 MHz, $CDCl_3$) δ 127.2 ($C_3$) ↔ δ 4.64 ($H_1$), δ 1.57 ($C_3$ *t*-Bu); δ 113.7 ($C_5$) ↔ δ 2.85 ($H_{7endo}$), δ 1.81 ($Me_5$), δ 0.73 ($H_{6exo}$); δ 112.5 ($Cp'^{t}$ *t*-Bu ring quaternary ) ↔ δ 5.37 ($Cp'^{t}$), δ 4.99 ($Cp'^{t}$), δ 4.80 ($Cp'^{t}$), δ 2.55 ($Cp'^{t}$ Me), δ 1.18 ($Cp'^{t}$ *t*-Bu); δ 102.3 ($Cp'^{t}$ Me ring quaternary) ↔ δ 5.37 ($Cp'^{t}$), δ 4.99 ($Cp'^{t}$), δ 4.80 ($Cp'^{t}$), δ 2.55 ($Cp'^{t}$ Me); δ 93.2 ($Cp'^{t}$) ↔ δ 4.99 ($Cp'^{t}$), δ 4.80 ($Cp'^{t}$), δ 2.55 ($Cp'^{t}$ Me); δ 88.0/87.9[a] ($C_{2/4}$) ↔ δ 5.68 ($H_4$), δ 5.28 ($H_2$), δ 2.85 ($H_{7endo}$), δ 1.81 ($Me_5$), δ 0.73 ($H_{6exo}$); δ 84.9 ($Cp'^{t}$) ↔ δ 5.37 ($Cp'^{t}$); δ 83.5 ($C_1$) ↔ δ 2.85 ($H_{7endo}$), δ 0.73 ($H_{6exo}$); δ 81.0 ($Cp'^{t}$) ↔ δ 5.37 ($Cp'^{t}$), δ 4.80 ($Cp'^{t}$); δ 37.7 ($C_7$) ↔ δ 5.28 ($H_2$), δ 1.90 ($H_{6endo}$), δ 0.73 ($H_{6exo}$); δ 35.8 ($C_3$ *t*-Bu quaternary) ↔ δ 1.57 ($C_3$ *t*-Bu); δ 35.3 ($C_6$) ↔ δ 5.68 ($H_4$), δ 5.28 ($H_2$), δ 4.64 ($H_1$), δ 2.85 ($H_{7endo}$), δ 1.81 ($Me_5$); δ 32.4 ($Cp'^{t}$ *t*-Bu quaternary) ↔ δ 1.18 ($Cp'^{t}$ *t*-Bu); δ 31.4 ($C_3$ *t*-Bu) ↔ δ 1.57 ($C_3$ *t*-Bu); δ 30.3 ($Me_5$) ↔ δ 5.68 ($H_4$); δ 29.8 ($C_3$ *t*-Bu) ↔ δ 1.18 ($C_3$ *t*-Bu); [a] Carbon signals overlap in spectrum. Analysis calculated for $C_{22}H_{34}BCoF_4$: C, 59.48; H, 7.71; found: C, 57.124; H, 7.541. Electrospray MS *m/z* calculated for $C_{22}H_{34}Co$ ($M^{+}$-$BF_4$): 357.199249; found: 357.198779.



**[(*t*-Bu-Me-$\mathrm{C_5H_3}$)Co(4,5-$\mathrm{Me_2}$-3-($\mathrm{CO_2Et}$)$\mathrm{C_7H_6}$)]$^+$ $\mathrm{BF_4^-}$ (357).** In the drybox, a flask was charged with Cp'Co($\mathrm{Cp'^{t}H}$) (**348**) (0.3719 g, 1.356 mmol) and removed to the Schlenk line, where dichloromethane (25 mL) was added. The solution was cooled to -78 °C and ethyl 2-butynoate (0.79 mL, 5 equiv) was added. Upon addition of $\mathrm{HBF_4{\bullet}Et_2O}$ (0.22 mL1.1 equiv), the color turned to green. Allowing the solution to warm to room temperature over several hours resulted in a color change to deep red. Removal of all volatile material gave a dark oily residue. The compound was purified by flash chromatography (silica gel) using 5% methanol-dichloromethane. After a red band was collected and the solvent was removed, there remained a red oily residue (0.1530 g, 24%). Recrystallization from dichloromethane/diethyl ether deposited a red liquid, impure by $^1$H NMR spectroscopy, although the identity of the minor compounds could not be ascertained. Small amounts of the major product could be obtained by careful, slow column chromoatograpy on silica gel, using dichloromethane and 1% ethanol/dichloromethane as the eluent. IR ($\mathrm{CDCl_3}$ cast, cm$^{-1}$) 3106 (w), 2965 (m), 1725 (s), 1652 (w), 1446 (m), 1385 (m), 1282 (s), 1244 (m), 1190 (m), 1055 (s), 866 (m), 533 (w), 521 (m); $^1$H NMR (360 MHz, $\mathrm{CDCl_3}$) δ 5.82 (t, $J$ = 2.1 Hz, $\mathrm{Cp'^{t}}$), 5.49 (dd, $J_{2\text{-}1}$ = 9.6 Hz, $J_{2\text{-}7exo}$ = 1.2 Hz, 1H, $\mathrm{H_2}$), 4.97 (dq, $J_{1\text{-}2}$ = 9.3 Hz, $J_{1\text{-}7exo} = J_{1\text{-}7endo} = J_{1\text{-}6endo}$ = 3.3 Hz, 1H, $\mathrm{H_1}$), 4.91 (t, $J$ = 2.3 Hz, 1H, $\mathrm{Cp'^{t}}$), 4.88 (t, $J$ = 2.7 Hz, 1H, $\mathrm{Cp'^{t}}$), 4.56 (dq, $J$ = 11.1, 7.1 Hz, 1H, $\mathrm{CO_2C\underline{H}_2CH_3}$), 4.50 (dq, $J$ = 11.0, 7.2 Hz, 1H, $\mathrm{CO_2C\underline{H}_2CH_3}$), 3.32 (dddd, $J_{7endo\text{-}7exo}$ = 18.0 Hz, $J_{7endo\text{-}6exo}$ = 12.3 Hz, $J_{7endo\text{-}6endo}$ = 7.2 Hz, $J_{7endo\text{-}1}$ = 3.0 Hz, 1H, $\mathrm{H_{7endo}}$), 2.49 (s, 3H, $\mathrm{Me_4}$), 2.40 (s, 3H, $\mathrm{Cp'^{t}}$Me), 2.36-2.22 (m, ddd by decoupling, $J_{7exo\text{-}7endo}$ = 17.6 Hz, $J_{7exo\text{-}6exo}$ = 4.6 Hz, $J_{7exo\text{-}1}$ = 3.3 Hz, 1H, $\mathrm{H_{7exo}}$), 1.86 (s, 3H, $\mathrm{Me_5}$), 1.45 (t, $J$ = 6.9 Hz, 3H, $\mathrm{CO_2CH_2C\underline{H}_3}$), 1.46-1.40 (m, 1H, $\mathrm{H_{6endo}}$), 1.17 (s, 9H, *t*-Bu ), 0.10 (ddd, $J_{6exo\text{-}6endo} = J_{6exo\text{-}7endo}$ = 12.3 Hz, $J_{6exo\text{-}7exo}$ = 4.8 Hz, 1H, $\mathrm{H_{6exo}}$); $^1$H-$^1$H GCOSY (300 MHz, $\mathrm{CDCl_3}$) δ 5.82 ($\mathrm{Cp'^{t}}$) ↔ δ 4.91$^a$ ($\mathrm{Cp'^{t}}$), δ 4.88$^a$ ($\mathrm{Cp'^{t}}$); δ 5.49 ($\mathrm{H_2}$) ↔ δ 4.97 ($\mathrm{H_1}$), δ 2.30 ($\mathrm{H_{7exo}}$); δ 4.97 ($\mathrm{H_1}$) ↔ δ 3.32 (w, $\mathrm{H_{7endo}}$), δ 2.30 ($\mathrm{H_{7exo}}$), δ 1.43 (w, $\mathrm{H_{6endo}}$); δ 4.56/4.50$^b$ ($\mathrm{CO_2C\underline{H}_2CH_3}$) ↔ δ 1.45 ($\mathrm{CO_2CH_2C\underline{H}_3}$);

δ 3.32 ($H_{7\mathrm{endo}}$) ↔ δ 2.30 ($H_{7\mathrm{exo}}$), δ 1.43 ($H_{6\mathrm{endo}}$), δ 0.10 ($H_{6\mathrm{exo}}$); δ 2.30$^{c}$ ($H_{7\mathrm{exo}}$) ↔ δ 0.10 ($H_{6\mathrm{exo}}$); δ 1.43 ($H_{6\mathrm{endo}}$) ↔ δ 0.10 ($H_{6\mathrm{exo}}$). [a]These signals overlap. [b] Two H atoms of the methylene are not resolved. [c] No observable cross peak to δ 1.43 ($H_{6\mathrm{endo}}$). $^{13}$C NMR (100 MHz, $CDCl_3$, $^{1}J_{CH}$ values obtained from HMQC spectrum) δ 167.9 (s, $\underline{C}O_2Et$), 115.0 (s, Cp$'^{t}$ *t*-Bu ring quaternary), 111.6 (s, $C_5$), 106.1 (s, $C_4$), 102.7 (s, Cp$'^{t}$ Me ring quaternary), 101.3 (s, $C_3$), 92.7 (d, $^{1}J_{CH}$ = 187 Hz, Cp$'^{t}$), 92.3 (d, $^{1}J_{CH}$ = 168 Hz, $C_2$), 90.1 (d, $^{1}J_{CH}$ = 156 Hz, $C_1$), 88.3 (d, $^{1}J_{CH}$ = 186 Hz, Cp$'^{t}$), 87.2 (d, $^{1}J_{CH}$ = 182 Hz, Cp$'^{t}$), 63.7 (t, $^{1}J_{CH}$ = 149 Hz, $CO_2\underline{C}H_2CH_3$), 42.3 (t, $^{1}J_{CH}$ = 125 Hz, $C_7$), 32.7 (t, $^{1}J_{CH}$ = 125 Hz, $C_6$), 32.3 (s, *t*-Bu quaternary), 29.7 (q, $^{1}J_{CH}$ = 129 Hz, *t*-Bu), 27.5 (q, $^{1}J_{CH}$ = 127 Hz, $Me_5$), 19.5 (q, $^{1}J_{CH}$ = 129 Hz, $Me_4$), 14.3 (q, $^{1}J_{CH}$ = 129 Hz, Cp$'^{t}$ Me), 14.1 (q, $^{1}J_{CH}$ = 127 Hz, $CO_2CH_2\underline{C}H_3$); HMQC (300 MHz, $CDCl_3$) δ 92.7 (Cp$'^{t}$) ↔ δ 5.82 (Cp$'^{t}$); δ 92.3 ($C_2$) ↔ δ 5.49 ($H_2$); δ 90.1 ($C_1$) ↔ δ 4.97 ($H_1$); δ 88.3 (Cp$'^{t}$) ↔ δ 4.88 (Cp$'^{t}$); δ 87.2 (Cp$'^{t}$) ↔ δ 4.91 (Cp$'^{t}$); δ 63.7 ($CO_2\underline{C}H_2CH_3$) ↔ δ 4.56 ($CO_2C\underline{H}_2CH_3$), δ 4.50 ($CO_2C\underline{H}_2CH_3$); δ 42.3 ($C_7$) ↔ δ 3.32 ($H_{7\mathrm{endo}}$), δ 2.28 ($H_{7\mathrm{exo}}$); δ 32.7 ($C_6$) ↔ δ 1.45 ($H_{6\mathrm{endo}}$), δ 0.10 ($H_{6\mathrm{exo}}$); δ 29.7 (*t*-Bu) ↔ δ 1.17 (*t*-Bu); δ 27.5 ($Me_5$) ↔ δ 1.86 ($Me_5$); δ 19.5 ($Me_4$) ↔ δ 2.49 ($Me_4$); δ 14.3 (Cp$'^{t}$ Me) ↔ δ 2.40 (Cp$'^{t}$ Me); δ 14.1 ($CO_2CH_2\underline{C}H_3$) ↔ δ 1.45 ($CO_2CH_2C\underline{H}_3$); HMBC (300 MHz, $CDCl_3$) δ 167.9 ($\underline{C}O_2Et$) ↔ δ 5.49 ($H_2$); δ 115.0 (Cp$'^{t}$ *t*-Bu ring quaternary) ↔ δ 5.82 (Cp$'^{t}$), δ 4.91 (Cp$'^{t}$), δ 2.40 (Cp$'^{t}$ Me), δ 1.17 (*t*-Bu); δ 111.6 ($C_5$) ↔ δ 2.49 ($Me_4$), δ 1.86 ($Me_5$), δ 0.10 ($H_{6\mathrm{exo}}$); δ 106.1 ($C_4$) ↔ δ 5.49 ($H_2$), δ 2.49 ($Me_4$), δ 1.86 ($Me_5$), δ 0.10 ($H_{6\mathrm{exo}}$); δ 102.7 (Cp$'^{t}$ Me ring quaternary) ↔ δ 5.82 (Cp$'^{t}$), δ 4.91 (Cp$'^{t}$), δ 2.40 (Cp$'^{t}$ Me); δ 101.3 ($C_3$) ↔ δ 2.49 ($Me_4$); δ 92.7 (Cp$'^{t}$) ↔ δ 4.91 (Cp$'^{t}$), δ 2.40 (Cp$'^{t}$ Me); δ 88.3 (Cp$'^{t}$) ↔ δ 5.82 (Cp$'^{t}$); δ 87.2 (Cp$'^{t}$) ↔ δ 5.82 (Cp$'^{t}$), δ 4.91 (Cp$'^{t}$); δ 63.7 ($CO_2\underline{C}H_2CH_3$) ↔ δ 1.45 ($CO_2CH_2C\underline{H}_3$); δ 42.3 ($C_7$) ↔ δ 5.49 ($H_2$), δ 0.10 ($H_{6\mathrm{exo}}$); δ 32.7 ($C_6$) ↔ δ 1.86 ($Me_5$); δ 32.3 (*t*-Bu quaternary) ↔ δ 1.17 (*t*-Bu); δ 29.7 (*t*-Bu) ↔ δ 1.17 (*t*-Bu). Analysis calculated for $C_{22}H_{32}BCoF_4O_2$: C, 55.72; H, 6.80; found: C, 58.852; H, 6.806.

Electrospray MS *m/z* calculated for $C_{22}H_{32}CoO_2$ ($M^+$-$BF_4$): 387.173428; found: 387.173272.

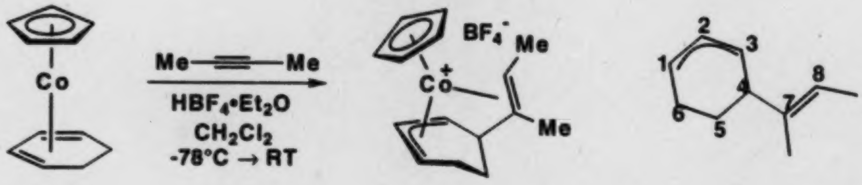


**358** **359A** **359B**

**[($\eta^5$-1-*t*-Bu-$C_5H_4$)Co($\eta^4$-2-*t*-Bu-5-Me-$C_5H_4$] (359A) and [($\eta^5$-1-*t*-Bu-$C_5H_4$)Co($\eta^4$-1-*t*-Bu-5-Me-$C_5H_4$] (359B).** To a suspension of (1-*t*-butyl$C_5H_4$)$_2$$Co^+$ $PF_6^-$ (**358**) (1.03 g, 2.31 mmol) in tetrahydrofuran (50 mL) at -78°C was added MeLi (1.8 mL, 1.4 M, ether, 1.1 equiv). The yellow suspension quickly turned into a red solution. After stirring at -78°C for 1h, the solution was warmed to room temperature and stirred an addition hour. The solvent was removed *in vacuo* and the residue was extracted with pentane under nitrogen. The extracts were filtered through Celite and the pentane was removed. A red oil (0.6816 g, 93%) remained. By $^1H$ NMR spectroscopy, this consisted of an approximately 8:1 mixture of isomers. The major isomer is identified as (1-*t*-butyl$C_5H_4$)Co(2-*t*-butyl-5-*exo*-methyl-1,3-cyclopentadiene). The minor isomer is tentatively identified as the 1,5-isomer. IR (hexane cast, $cm^{-1}$) 3096 (w), 3041 (m), 2955 (s), 2907 (s), 2864 (m), 1480 (m), 1460 (m), 1388 (m), 1359 (s), 1308 (w), 1277 (m), 1225 (w), 1199 (w), 1149 (w), 1129 (w), 1031 (m), 916 (m), 854 (w), 806 (m), 688 (w), 558 (w), 509 (w); $^1H$ NMR (360 MHz, $C_6D_6$) $\delta$ 4.92 (ddd, $J$ = 2.7, 1.6, 1.6 Hz, 1H, $Cp^t$), 4.88 (dd, $J$ = 2.8, 1.5 Hz, 1H, $H_3$), 4.71 (ddd, $J$ = 2.6, 2.6, 1.5 Hz, 1H, $Cp^t$), 4.37 (ddd, $J$ = 2.6, 1.6, 1.6 Hz, 1H, $Cp^t$), 3.78 (ddd, $J$ = 2.6, 2.6, 1.6 Hz, 1H, $Cp^t$), 2.67 (qdd, $J$ = 6.0, 2.4, 2.4 Hz, 1H, $H_5$), 2.56 (ddd, $J$ = 2.5, 2.5, 2.5 Hz, 1H, $H_4$), 2.52 (ddd, $J$ = 2.3, 2.3, 1.5 Hz, 1H, $H_1$), 1.26 (s, 9H, *t*-Bu), 1.22 (s, 9H, *t*-Bu), 0.32 (d, $J$ = 6.1 Hz, Me); $^{13}C$ NMR (75 MHz, $C_6D_6$) $\delta$ 112.3, 107.8, 79.0, 77.7, 76.3, 75.1, 71.3, 47.8, 45.0, 42.5, 31.9 (*t*-Bu), 31.1 (*t*-Bu), 27.1. *t*-Bu quaternary carbons are not located. MS *m/z* calculated for

$C_{19}H_{29}Co$ ($M^+$): 316.16013; found: 316.15927 (4 %). MS *m/z* calculated for $C_{15}H_{20}Co$ ($M^+ - t$-Bu): 259.08969; found: 259.08978 (100 %).

Data for minor compound: $^1$H NMR (360 MHz, $C_6D_6$) δ 5.00 (ddd, *J* = 2.4, 2.4, 1.5 Hz, 1H), 4.98 (apparent t, *J* = 2.7 Hz, 1H), 4.84 (br s, 1H), 4.67 (t, *J* = 2.5 Hz, 2H), 3.84 (apparent q, *J* = 1.9 Hz), 2.79 (qd, *J* = 5.9, 2.6 Hz, 1H), 2.41 (ddd, *J* = 3.0, 3.0, 1.8 Hz, 1H), 1.17 (s, 9H, t-Bu), 1.00 (s, 9H, t-Bu), 0.45 (d, *J* = 6.0 Hz, 3H, Me).

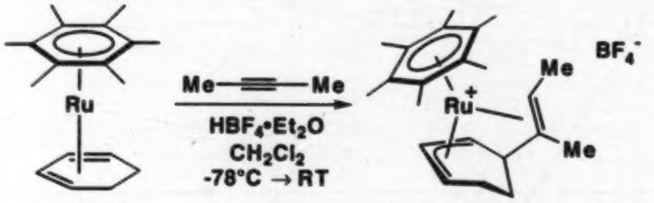


**360**

**361**

**[($C_5H_5$)Co($\eta^3$-$\eta^2$-4-(1,2-dimethylvinyl)-2-cyclohexen-1-yl)]$^+$ $BF_4^-$ (361).** To a Schlenk flask was added ($C_5H_5$)Co($\eta^4$-$C_6H_8$) (**360**) (0.5932 g, 2.906 mmol) and dichloromethane (30 mL). The red solution was cooled to -78 °C and 2-butyne (2 mL, 10 equiv) was added, followed by $HBF_4 \cdot Et_2O$ (0.47 mL, 1.1 equiv). The solution was allowed to warm slowly to room temperature. The solvent was reduced to 5 mL and the product precipitated by the addition of diethyl ether. A light orange-brown powder (0.9674 g, 96 %) was collected by filtration. The analytical sample was prepared by recrystallization from tetrahydrofuran/diethyl ether at -30 °C. IR ($CH_2Cl_2$ cast, $cm^{-1}$) 3121 (m), 2923 (m), 1448 (m), 1413 (m), 1383 (m), 1052 (s), 891 (m), 856 (m), 834 (m), 521 (m); $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 6.34 (br t, *J* = 5.6 Hz, 1H, $H_2$), 5.66 (br t, *J* = 5.3 Hz, 1H, $H_3$), 5.23 (q, *J* = 6.5 Hz, 1H, $H_8$), 5.13 (s, 5H, $C_5\underline{H}_5$), 5.20-5.10 (m, overlaps with Cp, 1H, $H_1$), 2.63 (br d, *J* = 14.9 Hz, 1H, $H_{6exo}$), 2.06 (d, *J* = 6.3 Hz, 3H, $Me_8$), 1.87 (s, 3H, $Me_7$), 1.68 (br s, 1H, $H_4$), 1.41 (br d, *J* = 15.1 Hz, 1H, $H_{6endo}$), 1.08 (br d, *J* = 15.8 Hz, $H_{5exo}$), 0.57 (br d, *J* = 16.0 Hz, 1H, $H_{5endo}$); 1H-$^1$H COSY (360 MHz, $CD_2Cl_2$) δ 6.34 ($H_2$) ↔ δ 5.66 ($H_3$), δ 2.63 ($H_{6exo}$), δ 1.41 ($H_{6endo}$); δ 5.66 ($H_3$) ↔ δ 1.08

($H_{5exo}$), δ 0.57 ($H_{5endo}$); δ 5.23 ($H_8$) ↔ δ 2.06 ($Me_8$), δ 1.87 (w, $Me_7$); δ 5.15 ($H_1$) ↔ δ 1.41 ($H_{6endo}$), δ 0.57 ($H_{5endo}$); δ 2.63 ($H_{6exo}$) ↔ δ 1.68 ($H_4$), δ 1.41 ($H_{6endo}$), δ 1.08 ($H_{5exo}$); δ 1.68 ($H_4$) ↔ δ 1.08 ($H_{5exo}$); δ 1.41 ($H_{6endo}$) ↔ δ 0.57 ($H_{5endo}$); δ 1.08 ($H_{5exo}$) ↔ δ 0.57 ($H_{5endo}$); $^{13}C$ NMR (100 MHz, $CD_2Cl_2$) δ 112.5 (s, $C_7$), 90.3 (d, $^1J_{CH}$ = 182.7 Hz, $\underline{C}_5H_5$), 88.5$^a$ (d, $^1J_{CH}$ = 165 Hz, $C_8$), 85.0 (d, $^1J_{CH}$ = 168.9 Hz, $C_1$), 82.7 (d, $^1J_{CH}$ = 163.9 Hz, $C_3$), 80.3 (d, $^1J_{CH}$ = 160.8 Hz, $C_2$), 43.0 (d, $^1J_{CH}$ = 136.1 Hz, $C_4$), 35.3 (t, $^1J_{CH}$ = 133.9 Hz, $C_6$), 25.0 (t, $^1J_{CH}$ = 132.9 Hz, $C_5$), 19.6 (q, $^1J_{CH}$ = 127.6 Hz, $Me_8$), 17.9$^b$ (q, $^1J_{CH}$ = 127.7 Hz, $Me_7$), $^a$Signal overlaps with $C_5H_5$ signal in gated decoupled spectrum. $^b$Signal is distorted. $^1H$-$^{13}C$ HETCORR (100 MHz, $CD_2Cl_2$) δ 90.3 ($\underline{C}_5H_5$) ↔ δ 5.13 ($C_5\underline{H}_5$); δ 88.5 ($C_8$) ↔ δ 5.23 ($H_8$); δ 85.0 ($C_1$) ↔ δ 5.15 ($H_1$); δ 82.7 ($C_3$) ↔ δ 5.66 ($H_3$); δ 80.3 ($C_2$) ↔ δ 6.34 ($H_2$); δ 43.0 ($C_4$) ↔ δ 1.68 ($H_4$); δ 35.3 ($C_6$) ↔ δ 2.63 ($H_{6exo}$), δ 1.41 ($H_{6endo}$); δ 25.0 ($C_5$) ↔ δ 1.08 ($H_{5exo}$), δ 0.57 ($H_{5endo}$); δ 19.6 ($Me_8$) ↔ δ 2.06 ($Me_8$); δ 17.9 ($Me_7$) ↔ δ 1.87 ($Me_7$). Analysis calculated for $C_{15}H_{20}BCoF_4$: C, 52.06; H, 5.83; found: C, 51.685; H, 5.947.



362 363

**[($C_6Me_6$)Ru($\eta^3$-$\eta^2$-4-(1,2-dimethylvinyl)-2-cyclohexen-1-yl)]$^+$ $BF_4^-$ (363).** To a Schlenk flask was added ($C_6Me_6$)Ru($\eta^4$-$C_6H_8$) (**362**) (0.0689 g, 0.201 mmol) and dichloromethane (8 mL). The red solution was cooled to -78 °C and 2-butyne (0.16 mL, 10 equiv) was added, followed by $HBF_4$•$Et_2O$ (33 μL, 1.1 equiv). The solution was allowed to warm slowly to room temperature. The solvent was reduced to 5 mL and the product precipitated by the addition of diethyl ether. The ruthenium complex slowly decomposed, preventing an accurate yield measurement. Estimated yield was about 60%

of impure yellow powder. $^1$H NMR (CD$_2$Cl$_2$, 300 MHz) δ 4.05 (m, dddd, $J_{1\text{-}2}$ = 7.1 Hz, $J_{1\text{-}6\text{exo}}$ = 4.3 Hz, $J_{1\text{-}3}$ = $J_{1\text{-}5\text{exo}}$ = 1.4 Hz, 1H, H$_1$), 3.96 (q, $J$ = 6.4 Hz, 1H, H$_8$), 3.74 (ddddd, $J_{3\text{-}2}$ = 7.0 Hz, $J_{3\text{-}5\text{exo}}$ = 5.6 Hz, $J_{3\text{-}1}$ = 1.4 Hz, $J_{3\text{-}5\text{endo}}$ = $J_{3\text{-}4}$ = small, 1H, H$_3$), 3.35 (ddd, $J_{2\text{-}1}$ = 7.1 Hz, $J_{2\text{-}3}$ = 6.7 Hz, $J_{2\text{-}6\text{exo}}$ = 0.8 Hz, 1H, H$_2$), 2.45 (dddd, $J_{6\text{exo-}6\text{endo}}$ = 14.1 Hz, $J_{6\text{exo-}1}$ = 3.6 Hz, $J_{6\text{exo-}5\text{exo}}$ = $J_{6\text{exo-}5\text{endo}}$ = 1.7 Hz, 1H, H$_{6\text{exo}}$), 2.13 (s, 18H, C$_6\underline{\text{Me}}_6$), 1.87 (br m, overlap with δ 1.85, 1H, H$_4$), 1.85 (m, 1H, H$_{6\text{endo}}$), 1.82 (d, $J$ = 6.4 Hz, 3H, Me$_8$), 1.69 (s, 3H, Me$_7$), 1.03 (m, 1H, H$_{5\text{exo}}$), 0.92 (br d, $J$= 14.7Hz, 1H, H$_{5\text{endo}}$); Decoupling (400 MHz, CD$_2$Cl$_2$) Irr δ 2.45 ↔ δ 4.05 (dt, $J$ = 5.5, 1.6 Hz), δ 1.03 (dt, $J$ = 14.7, 4.0 Hz), δ 3.74 (lost small $J$); Irr δ 1.03 ↔ δ 0.92 (br m), δ 3.74 (br d, $J$ = 7.0 Hz), δ 2.45 (dt, $J$ = 14.1, 4.8 Hz), δ 3.35 (lose small $J$); Irr δ 3.35 ↔ δ 3.74 (d, $J$ = 4.2 Hz), δ 4.05 (d, $J$ = 4.3 Hz), δ 2.45 (lost small $J$); Irr δ 3.74 ↔ δ 4.05 (lost small $J$ ), δ 3.35 (d, $J$ = 6.9 Hz), δ 1.03 (br d), δ 0.92 (narrower); Irr δ 3.96 ↔ δ 1.82 (s); Irr δ 4.05 ↔ δ 3.74 (apparent t ), δ 3.35 (d, $J$ = 6.7 Hz), δ 2.45 (ddd, $J$ = 14.3, 4.3, 2.5 Hz), δ 1.03 (changes); Irr δ 0.92 ↔ δ 3.74 (changes), δ 4.05 (lost small $J$), δ 2.45 (lost small $J$); Irr δ 1.85 ↔ δ 0.92 (narrower), δ 1.03 (dd, $J$ = 14.7, 4.3 Hz), δ 2.45 (br d, $J$ = 4.8 Hz), δ 3.74 (changes); $^1$H-$^1$H COSY (400 MHz, CD$_2$Cl$_2$) δ 4.05 (H$_1$) ↔ δ 3.74 (w, H$_3$), δ 3.35 (H$_2$), δ 2.45 (H$_{6\text{exo}}$), δ 1.85 (H$_{6\text{endo}}$); δ 3.96 (H$_8$) ↔ δ 1.82 (Me$_8$); δ 3.74 (H$_3$) ↔ δ 3.35 (H$_2$), δ 1.03 (w, H$_{5\text{exo}}$), δ 0.92 (H$_{5\text{endo}}$); δ 2.45 (H$_{6\text{exo}}$) ↔ δ 1.85 (H$_{\text{endo}}$); δ 1.86 (H$_4$ and H$_{6\text{endo}}$) ↔ δ 1.03 (H$_{5\text{exo}}$), δ 0.92 (H$_{5\text{endo}}$); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 106.5 (s, $\underline{\text{C}}_6$Me$_6$), 100.8 (s, C$_7$), 81.9 (d, $^1J_{\text{CH}}$ = 165.6 Hz, C$_2$), 74.0 (d, $^1J_{\text{CH}}$ = 154.0 Hz, C$_1$), 73.2 (d, $^1J_{\text{CH}}$ = 154.9 Hz, C$_8$), 66.2 (d, $^1J_{\text{CH}}$ = 169.5 Hz, C$_3$), 43.6 (d, $^1J_{\text{CH}}$ = 129.4 Hz, C$_4$), 36.2 (t, $^1J_{\text{CH}}$ = 126.6 Hz, C$_6$), 23.5 (t, $^1J_{\text{CH}}$ = 130.4 Hz, C$_5$), 18.0 (q, $^1J_{\text{CH}}$ = 124.6 Hz, Me$_8$), 16.70 (q, $^1J_{\text{CH}}$ = 129 Hz, C$_6\underline{\text{Me}}_6$), 16.69 (q, $^1J_{\text{CH}}$ = 129.3 Hz, Me$_7$); HMBC (400 MHz, CD$_2$Cl$_2$) δ 81.9 (C$_2$) ↔ δ 3.35 (H$_2$); δ 74.0 (C$_1$) ↔ δ 4.05 (H$_1$); δ 66.2 (C$_3$) ↔ δ 3.74 (H$_3$); δ 43.6 (C$_4$) ↔ δ 1.87 (H$_4$); δ 36.2 (C$_6$) ↔ δ 2.45 (H$_{6\text{exo}}$), δ 1.85 (H$_{6\text{endo}}$); δ 23.5 (C$_5$) ↔ δ 1.03 (H$_{5\text{exo}}$), δ 0.92 (H$_{5\text{endo}}$); δ 18.0 (Me$_8$) ↔ δ 1.82 (Me$_8$); δ 16.70 (C$_6\underline{\text{Me}}_6$) ↔ δ 2.13 (C$_6\underline{\text{Me}}_6$); δ 16.69 (Me$_7$) ↔ δ 1.69 (Me$_7$).

## Notes and References

1. Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemisty*; University Science: Mill Valley, California, 1987.
2. Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*, Wadsworth, Inc: Belmont, California, 1984.
3. Noyori, R., in *Transition Metal Organometallics in Organic Synthesis*, Alper, H., Ed. Academic Press: New York, 1976, Chapter 2, pp 83-197.
4. Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081.
5. (a) Dyker, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2223. (b) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259. (c) Malacria, M. *Chem. Rev.* **1996**, *96*, 289. (d) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, D. J. *Chem. Rev.* **1996**, *96*, 635. (e) Dell, C. P. *Contemp. Org. Synth.* **1997**, *4*, 87. (f) Hegedus, L. S. *Coord. Chem. Rev.* **1997**, *161*, 129. (g) Naota, T.; Takaya, H.; Murahashi, S.-I. *Chem. Rev.* **1998**, *98*, 2599. For a lead review on cycloisomerizations, see: (h) Trost, B. M.; Krische, M. J. *Synlett* **1998**, 1.
6. Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49.
7. Fruhauf, H.-W. *Chem. Rev.* **1997**, *97*, 523.
8. (a) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411-32. (b) Brookhart, M.; Studabaker, W. B.; Husk, G. R. *Organometallics* **1987**, *6*, 1141. (c) Brookhart, M.; Studabaker, W. B.; Humphrey, M. B.; Husk, G. R. *Organometallics* **1989**, *8*, 132. (d) Brookhart, M.; Liu, Y. *Organometallics* **1989**, *8*, 1572. (e) Guerchais, V.; Astruc, D.; Nunn, C. M.; Cowley, A. H. *Organometallics* **1990**, *9*, 1036. (f) Brookhart, M.; Liu, M.; Goldman, E. W.; Timmers, D. A.; Williams, G. D. *J. Am. Chem. Soc.* **1991**, *113*, 927. (g)

Brookhart, M.; Liu, Y. *J. Am. Chem. Soc.* **1991**, *113*, 939. Casey, C. P.; Smith-Vosejpka, L. J. *Organometallics* **1992**, *11*, 738. (h) Guerchais, V.; Levesque, S.; Hornfeck, A.; Lapionte, C.; Sinbandhit, S. *Organometallics* **1992**, *11*, 3926. (i) Seitz, W. J.; Saha, A. K.; Hossain, M. M. *Organometallics* **1993**, *12*, 2604.

9. Reviews: (a) Dotz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Wulff, W. D.; Yang, D. C.; Murray, C. K. *Pure Appl. Chem.* **1988**, *60*, 137. (c) Reissig, H.-U. *Top. Curr. Chem.* **1988**, *144*, 73. (d) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 1065. See also reference 7 and references cited therein.

10. (a) Mitsudo, T.; Kokuryo, K.; Takegami, Y. *J. Chem. Soc., Chem. Commun.* **1976**, 722. (b) Mitsudo, T.; Kokuryo, K.; Shinsugi, T.; Nakagawa, Y.; Watanabe, Y.; Takegami, Y. *J. Org. Chem.* **1979**, *44*, 4492. (c) Rosenblum, M.; Scheck, D. *Organometallics* **1982**, *1*, 397. (d) Ville, G. A.; Vollhardt, K. P. C.; Winter, M. J. *Organometallics* **1984**, *3*, 1177 and references therein. (e) Mitsudo, T.; Hori, Y.; Watanabe, Y. *J. Organomet. Chem.* **1987**, *334*, 157. (f) Trost, B. M.; Grese, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 7363. (g) Trost, B. M.; Grese, T. A. *J. Org. Chem.* **1992**, *57*, 686. (h) Trost, B. M.; Yanai, M.; Hoogsteen, K. *J. Am. Chem. Soc.* **1993**, *115*, 5294. (i) Mitsudo, T.; Naruse, H.; Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 580.

11. (a) Pauson, P. L.; Khand, I. U. *Ann. N. Y. Acad. Sci.***1977**, *295*, 2. (b) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855. (c) Schore, N. E.; *Org. React.* **1991**, *40*, 1. (d) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 1037. (e) Schore, N. E. In *Comprehensive Organometallic Chemistry II* ; Abel, E. W., Stone, F. G. A., Silkinson, G., Eds.; Elsevier: New York, 1995; Vol 12, p 703. (f) Geis, O.; Schmalz, H.-G. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 911. See also reference 4. Recent examples: (g) Krafft, M. E.; Wilson, A. M.; Dasse, O. A.; Shao, B.;

Cheung, Y. Y.; Fu, Z.; Bonaga, L. V. R.; Mollman, M. K. *J. Am. Chem. Soc.* **1996**, *118*, 6080. (h) Fonquerna, S.; Moyano, A.; Pericas, M. A.; Riera, A. *J. Am. Chem. Soc.* **1997**, *119*, 10225. (i) Sugihara, T.; Yamada, M.; Ban, H.; Yamaguchi, M.; Kaneko, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2801. (j) Rajesh, T.; Periasamy, M. *Tetrahedron Lett.* **1998**, *39*, 117. (k) Kim, J. W.; Chung, Y. K.; *Synthesis* **1998**, 142. (l) Rutherford, D. T.; Christie, S. D. R. *Tetrahedron Lett.* **1998**, *39*, 9805. (m) Sugihara, T.; Yamaguchi, M. *J. Am . Chem. Soc.* **1998**, *120*, 10782. (n) Morimoto, T.; Chatani, N.; Murai, S. *J. Am. Chem. Soc.* **1999**, *121*, 1758.

12. Ti: (a) Hicks, F. A.; Berk, S. C.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 2713. (b) Hicks, F. A.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 9450. (c) Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 11688. Zr: (d) Negeshi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. W: (e) Hoye, T. R.; Suriano, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 1154. Cr: (f) Jordi, L.; Segundo, A.; Camps, F.; Ricart, S.; Moreto, J. M. *Organometallics* **1993**, *12*, 3795. Mo: (g) Jeong, N.; Lee, S. J.; Lee, B. Y.; Chung, Y. K. *Tetrahedron Lett.* **1993**, *34*, 4027. Fe: (h) Pearson, A. J.; Dubbert, R. A. *Organometallics* **1994**, *13*, 1656. (i) Pearson, A. J.; Perosa, A. *Organometallics* **1995**, *14*, 5178. Ru: (j) Morimoto, T.; Chatani, N.; Fukumoto, Y.; Y.; Murai, S. *J. Org. Chem.* **1997**, *62*, 3762. (k) Kondo, T.; Suzuki, N.; Okada, T.; Mitsudo, T. *J. Am. Chem. Soc.* **1997**, *119*, 6187. (l) Chatani, N.; Morimoto, T.; Fukumoto, Y.; Murai, S. *J. Am. Chem. Soc.* **1998**, *120*, 5335. Rh: (m) Koga, Y.; Kobayashi, T.; Narasaka, K. *Chem. Lett.* **1998**, 249. (n) Jeong, N.; Lee, S.; Sung, B. K. *Organometallics* **1998**, *17*, 3642.

13. (a) Rautenstrauch , V.; Megard, P.; Conesa, J.; Kuster, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1413. (b) Pagenkopf, B. L.; Livingstone, T. *J. Am. Chem. Soc.*

**1996**, *118*, 2285. (c) Jeong, N.; Hwang, S. H.; Lee, Y. W.; Lim, J. S. *J. Am. Chem. Soc.* **1997**, *119*, 10549.

14. Fe: (a) Bakhtiar, R.; Drader, J. J.; Jacobson, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 8304. (b) Gilbertson, S. R.; Zhao, X.; Dawson, D. P.; Marshall, K. L. *J. Am. Chem. Soc.* **1993**, *115*, 8517. Ni: (c) Wender, P. A.; Smith, T. E. *J. Org. Chem.* **1995**, *60*, 2962. (d) Suisse, I.; Bricout, H.; Mortreux, A. *Tetrahedron Lett.* **1995**, *36*, 5011. Rh: (e) Jolly, R. S.; Luedtke, G.; Sheehan, D.; Livinghouse, T. *J. Am. Chem. Soc.* **1990**, *112*, 4965. (f) McKinstry, L.; Livinghouse, T. *Tetrahedron Lett.* **1994**, *50*, 6145. (g) Wender, P. A.; Jenkins, T. E.; Suzuki, S. *J. Am. Chem. Soc.* **1995**, *36*, 5011. Pd: (h) Mandai, T.; Suzuki, S.; Ikawa, A.; Murakami, T.; Kaweda, M.; Tsuji, J. *Tetrahedron Lett.* **1991**, *32*, 7687. (i) Inanaga, J.; Sugimoto, Y.; Hanamoto, T. *Tetrahedron Lett.* **1992**, *33*, 7035.

15. (a) Wulff, W. D.; Powers, T. S. *J. Org. Chem.* **1993**, *58*, 2381. (b) Rahm, A.; Wulff, W. D.; Rheingold, A. L. *Organometallics* **1993**, *12*, 597. (c) Dotz, K. H.; Noack, R.; Harms, K.; Muller, G. *Tetrahedron* **1990**, *46*, 1235. (d) Dotz, K. H.; Tiriliomis, A.; Harms, K. *Tetrahedron* **1993**, *25*, 5577. (e) Christoffers, J.; Dotz, K. H. *Chem. Ber.* **1995**, *128*, 157.

16. Reviews: (a) Dotz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644. (b) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. (c) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271. See also reference 9. Recent examples: (d) Waters, M. L.; Brandvold, T. A.; Issacs, L.; Wulff, W. D.; Rheingold, A. L. *Organometallics* **1998**, *17*, 4298. (e) Wang, H.; Wulff, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 10573.

17. (a) Reppe, W.; Schlichting, O.; Klager, K.; Teopel, T. *Liebigs Ann. Chem.* **1948**, *560*, 1. (b) Colborn, R. E.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 5470. (c) Lawrie, C. J.; Gable, K. P.; Carpender, B. K. *Organometallics* **1989**, *8*, 2274. Application: (d) Boussie, T. R.; Streitwieser, A. J. *J. Org. Chem.* **1993**, *58*,

2377. Early review: (e) Jolly, P. W. In Comprehensive Organometallic Chemistry; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon: London, 1982; Vol. 8, p 649. See also: (f) Rigby, J. H.; Warshakoon, N. C. *Tetrahedron Lett.* **1997**, *38*, 2049.

18. (a) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. (b) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (c) Bonnemann, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248. (d) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 1129. (d) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Silkinson, G., Eds.; Elsevier: New York, 1995; Vol 12, p 741. See also references 4, 6 and 7.

19. (a) Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1998**, *120*, 1672 and references therein. (b) Tsuda, T.; Mizuno, H.; Takeda, A.; Tobisawa, A. *Organometallics* **1997**, *16*, 932. (c) Varela, J. A.; Castedo, L.; Saa, C. *J. Org. Chem.* **1997**, *62*, 4189. (d) Johnson, E. S.; Balaich, G. J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 7685. (e) Yamamoto, Y.; Kitahara, H.; Hattori, R.; Itoh, K. *Organometallics* **1998**, *17*, 1910. (f) Sigman, M. S.; Fatland, A. W.; Eaton, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 5130. (g) Yang, J.; Verkade, J. G. *J. Am. Chem. Soc.* **1998**, *120*, 6834. (h) Pena, D.; Escudero, S.; Perez, D.; Guitan, E.; Castedo, L. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2659. (i) Diercks, R.; Eaton, B. E.; Gurtzgen, S.; Jalisatgi, S.; Matzger, A. J.; Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1998**, *120*, 8247. (j) Varela, J. A.; Castedo, L.; Saa, C. *J. Am. Chem. Soc.* **1998**, *120*, 12147. (k) Seo, J.; Chui, H. M. P.; Heeg, M. J.; Montgomery, J. *J. Am. Chem. Soc.* **1999**, *121*, 476. For [2 + 2 + 1] trimerizations of alkynes see: (l) O'Connor, J. M.; Hiibner, K.; Merwin, R.; Gantzel, P. K.; Fong, B. S.; Adams, M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 3631.

20. Mo: (a) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5426. (b) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 7324. (c) Forbes, M. D. E.; Patton, J. T.; Myers, T. L.; Maynard, H. D.; Smith, D. W., Jr.; Schulz, G. R.; Wagener, K. B. *J. Am. Chem. Soc.* **1992**, *114*, 10978. (d) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 3800. Ru: (e) Kim, S.-H.; Bowden, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10801. (f) Kim, S.-H.; Zuercher, W. J.; Bowden, N. B.; Grubbs, R. H. *J. Org. Chem.* **1996**, *61*, 1073. (g) Miller, S. J.; Blackwell, H. E.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 9606. See also: (h) Grubbs, R. H.; Pine, S. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 1115. (i) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446.

21. Heck reaction reviews: (a) Heck, R. F., In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 4, p 833. (b) de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379. (c) Crisp, G. T. *Chem. Soc. Rev.* **1998**, *27*, 427. (d) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047. See also (e) Mehnert, C. P.; Weaver, D. W.; Ying, J. Y. *J. Am. Chem. Soc.* **1998**, *120*, 12289 and references therein. Use in seven membered ring synthesis: (f) Ma, S.; Negeshi, E. *J. Org. Chem.* **1994**, *59*, 4730. (g) Negeshi, E.; Ma, S.; Sugihara, T.; Noda, Y. *J. Org. Chem.* **1997**, *62*, 1922.

22. El Ali, B.; Okuro, K.; Vasapollo, G.; Alper, H. *J. Am. Chem. Soc.* **1996**, *118*, 4264.

23. (a) Sato, Y.; Takimoto, M.; Hayashi, K.; Katsuhara, T.; Takagi, K.; Mori, M. *J. Am. Chem. Soc.* **1994**, *116*, 9771. (b) Ikeda, S.; Mori, N.; Sato, Y. *J. Am. Chem. Soc.* **1997**, *119*, 4779. (c) Mori, N.; Ikeda, S.; Sato, Y. *J. Am. Chem. Soc.* **1999**, *121*, 2722.

24. (a) Huffman, M. A.; Liebeskind, L. S. *Organometallics* **1992**, *11*, 255. (b) Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 4895.

25. Seven-membered ring containing natural products: Fischer, N. H.; Olivier, E. J.; Fischer, H. D. *Fortschr. Chem. Org. Naturst.* **1979**, *38*, 47. Heathcock, C. H.; Graham, S. L.; Pirrung, M. C.; Pavoac, F.; White, C. T. In *Total Synthesis of Natural Products*; Apsimon, J., Ed.; John Wiley and Sons: New York, 1983; Vol. 5, p 333. Rigby, J. H. In *Studies in Natural Products Chemistry*; Atta-ur-Rahman, Ed.; Elsevier Science Publishers B. V.: Amsterdam, 1988; Vol 12, p 233. Fraga, B. M. *Nat. Prod. Rep.* **1996**, *13*, 307. See also: Kim, S.; Winkler, J. D. *Chem. Soc. Rev.* **1997**, *26*, 387 and references therein.

26. Greco, A.; Carbonaro, A.; Dall'Asta, G. *J. Org. Chem.* **1970**, *35*, 271. (b) Takahashi, A.; Inukai, T. *J. Chem. Soc., Chem. Commun.* **1970**, 1473. (c) Lyons, J. E.; Myers, H. K.; Schneider, A. *Ann. N. Y. Acad. Sci.* **1980**, *333*, 273. (d) Lautens, M.; Tam, W.; Sood, C. *J. Org. Chem.* **1993**, *58*, 4513. (e) Chen, Y.; Snyder, J. K. *J. Org. Chem.* **1998**, *63*, 2060.

27. Lautens, M.; Tam, W.; Lautens, J. C.; Edwards, L. G.; Crudden, C. M.; Smith, A. C. *J. Am. Chem. Soc.* **1995**, *117*, 6863.

28. (a) Wang, C.; Lang, M. G.; Sheridan, J. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 3236. (b) Wang, C.; Sheridan, J. B.; Chung, H.; Cote, M. L.; Lalancette, R. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 8966. (c) Chaffee, K.; Huo, P.; Sheridan, J. B.; Barbieri, A.; Aistars, A.; Lalancette, R. A.; Ostrander, R. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1995**, *117*, 1900. (d) Chen, W.; Chung, H.; Wang, C.; Sheridan, J. B.; Cote, M. L.; Lalancette, R. A. *Organometallics* **1996**, *15*, 3337. (e) Chung, H.; Sheridan, J. B.; Cote, M. L.; and Lalancette, R. A. *Organometallics* **1996**, *15*, 4575. (f) Chen, W.; Chaffee, K.; Chung, H.; Sheridan, J. B. *J. Am. Chem. Soc.* **1996**, *118*, 9980.

29. (a) Rigby, J. H. *Acc. Chem. Res.* **1993**, *26*, 579. (b) Rigby, J. H.; Pigge, F. C. *Synlett* **1996**, 631. (c) Rigby, J. H.; Rege, S. D.; Sandanayaka, V. P.; Kirova, M. *J. Org. Chem.* **1996**, *61*, 842. (d) Rigby, J. H.; Warshakoon, N. C.; Heeg, M. J. *J.*

*Am. Chem. Soc.* **1996**, *118*, 6094. (e) Rigby, J. H.; Kirova, M.; Niyaz, N.; Mohammadi, F. *Synlett* **1997**, 805. (f) Rigby, J. H. *Org. React.* **1997**, *49*, 331. (g) Rigby, J. H.; Fales, K. R. *Tetrahedron Lett.* **1998**, *39*, 5715. (h) Rigby, J. H.; Hu, J.; Heeg, M. J. *Tetrahedron Lett.* **1998**, *39*, 2265. (g) Rigby, J. H.; Fales, K. R. *Tetrahedron Lett.* **1998**, *39*, 1525.

30. (a) Binger, P.; Buch, H. M. *Top. Curr. Chem.* **1979**, *135*, 77. (b) Binger, P.; Schuchardt, U. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 706.
31. Trost, B. M.; Nanninga, T. N.; Chan, D. M. T. *Organometallics* **1982**, *1*, 1543.
32. Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 62.
33. Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 819.
34. Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 1.
35. Mann, J. *Tetrahedron* **1986**, *42*, 4611.
36. (a) Chan, D. M. T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 271. (b) Hosomi, A.; Tominaga, Y. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 593. (c) Harrington, P. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Silkinson, G., Eds.; Elsevier: New York, 1995; Vol 12, p 923.
37. (a) Harmata, M. *Tetrahedron* **1997**, *53*, 6235. Recent example: (b) Wang, Y.; Arif, A. M.; West, F. G. *J. Am. Chem. Soc.* **1999**, *121*, 876.
38. Rigby, J. H.; Pigge, F. C. *Org. React.* **1997**, *51*, 351.
39. (a) Trost, B. M.; Schneider, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 213. (c) Trost, B. M.; Matelich, M. C. *J. Am. Chem. Soc.* **1991**, *113*, 9007. (d) Trost, B. M.; Marrs, C. M. *J. Am. Chem. Soc.* **1993**, *115*, 6636.
40. (a) Trost, B. M.; MacPherson, D. T. *J. Am. Chem. Soc.* **1987**, *109*, 3483. (b) Trost, B. M.; Yamazaki, S. *Chem. Lett.* **1994**, 2245.

41. (a) Trost, B. M.; Grese, T. A. *J. Org. Chem.* **1992**, *57*, 686. (b) Trost, B. M.; Higuchi, R. I. *J. Am. Chem. Soc.* **1996**, *118*, 10094.

42. (a) Trost, B. M.; Seoane, P.; Mignani, S.; Acemoglu, M. *J. Am. Chem. Soc.* **1989**, *111*, 7487. (b) Trost, B. M.; Grese, T. A.; Chan, D. M. T. *J. Am. Chem. Soc.* **1991**, *113*, 7350. (c) Trost, B. M.; Grese, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 7363.

43. (a) Herndon, J. W.; Chatterjee, G.; Patel, P. P.; Matasi, J. J.; Tumer, S. U.; Harp, J. J.; Reid, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 7808. (b) Herndon, J. W.; Zora, M.; Patel, P. P.; Chatterjee, G.; Matasi, J. J.; Tumer, S. U. *Tetrahedron* **1993**, *49*, 5507.

44. Reviews: (a) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1. (b) Wong, H. N. C.; Hon, M. Y.; Tse, C. W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165. (c) Piers, E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 971. (d) Hudlicky, T.; Fan, R.; Reed, J. W.; Gadamasetti, K. G. *Org. React.* **1992**, 41, 1.

45. (a) Wulff, W. D.; Yang, D. C.; Murray, C. K. *J. Am. Chem. Soc.* **1988**, 110, 2653. (b) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642.

46. (a) Barluenga, J.; Aznar, F.; Martin, A. *Organometallics* **1995**, *14*, 1429. (b) Barluenga, J.; Aznar, F.; Martin, A.; Vazquez, J. T. *J. Am. Chem. Soc.* **1995**, *117*, 9419. (c) Barluenga, J.; Tomas, M.; Ballesteros, A.; Santamaria, J.; Carbajo, R. J.; Lopez-Ortiz, F.; Garcia-Granda, S.; Pertierra, P. *Chem. Eur. J.* **1996**, *2*, 88. (d) Barluenga, J.; Tomas, M.; Rubio, E.; Lopez-Ortiz, F.; Garcia-Granda, S.; Pertierra, P. *J. Am. Chem. Soc.* **1996**, *118*, 695. (e) Barluenga, J.; Tomas, M.; Bieger, K.; Garcia-Grande, S.; Santiago-Garcia, R. *J. Organomet. Chem.* **1997**, *529*, 233. (f) Barluenga, J.; Aznar, F.; Fernandez, M. *Chem. Eur. J.* **1997**, *3*,

1629. (g) Barlenga, J.; Tomas, M.; Rubio, E.; Lopez-Pelegrin, J. A.; Garcia-Granda, S.; Priede, M. P. *J. Am. Chem. Soc.* **1999**, *121*, 3065.

47. Davies, H. M. L. *Tetrahedron* **1993**, *49*, 5203 and references therein.

48. Recent publications: (a) Davies, H. M. L.; Matasi, J. J.; Hodges, L. M.; Huby, N. J. S.; Thornley, C.; Kong, N.; Houser, J. H. *J. Org. Chem.* **1997**, *62*, 1095 and references therein. (b) Davies, H. M. L.; Doan, B. D. *J. Org. Chem.* **1998**, *63*, 657. (c) Davies, H. M. L.; Stafford, D. G.; Doan, B. D.; Houser, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 3326. (d) Davies, H. M. L.; Hodges, L. M.; Thornley, C. T. *Tetrahedron Lett.* **1998**, *39*, 2707. (e) Davies, H. M. L.; Hodges, L. M.; Matasi, J. J.; Hansen, T.; Stafford, D. G. *Tetrahedron Lett.* **1998**, *39*, 4417. (f) Davies, H. M. L.; Cao, G. *Tetrahedron Lett.* **1998**, *39*, 5943. (e)

49. (a) Padwa, A.; Krumpe, K. E.; Gareau, Y.; Chiacchio, U. *J. Org. Chem.* **1991**, *56*, 2523. (b) Padwa, A.; Hornbuckle, S. F.; Fryxell, G. E.; Zhang, Z. J. *J. Org. Chem.* **1992**, *57*, 5747. (c) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091.

50. (a) Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 5066. (b) Harvey, D. F.; Grenzer, E. M.; Gantzel, P. K. *J. Am. Chem. Soc.* **1994**, *116*, 6719.

51. Harvey, D. F.; Brown, M. F. *J. Org. Chem.* **1992**, *57*, 5559.

52. (a) Wender, P. A.; Takahashi, H.; Witulski, B. *J. Am. Chem. Soc.* **1995**, *117*, 4720. (b) Wender, P. A.; Husfeld, C. O.; Langkopf, E.; Love, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 1940. (c) Wender, P. A.; Sperandio, D. *J. Org. Chem.* **1998**, *63*, 4164. (d) Wender, P. A.; Husfeld, C. O.; Langkopf, E.; Love, J. A.; Pleuss, N. *Tetrahedron* **1998**, *54*, 7203.

53. Wender, P. A.; Rieck, H.; Fuji, M. *J. Am. Chem. Soc.* **1998**, *120*, 10976.

54. Binger, P. A.; Wedemann, P.; Kozhushkov, S. I.; de Meijere, A. *Eur. J. Org. Chem.* **1998**, 113.

55. Chatani, N.; Kataoka, K.; Murai, S.; Furukawa, N.; Seki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9104. see also: Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6049.

56. (a) Kreiter, C. G.; Koch, E.-C., Frank, W.; Reiß, G. *Inorg, Chim. Acta.* **1994**, *220*, 77. (b) Kreiter, C. G.; Fiedler, C.; Frank, W.; Reiß, G. *Chem. Ber.* **1995**, *128*, 515.

57. (a) Hubel, W.; Braye, E. H. *J. Inorg. Nucl. Chem.* **1959**, *10*, 250. (b) Weiss, E.; Hubel, W. *Chem. Ber.* **1962**, *95*, 1179. (c) Braye, E. H.; Hubel, W. *J. Organometal. Chem.* **1965**, *3*, 25. See also: (d) Dickson, R. S.; Michel, L. J. *Aust. J. Chem.* **1975**, *28*, 285. (e) Foust, D. F.; Rausch, M. D. *J. Organometal. Chem.* **1982**, *239*, 321.

58. Cooke, J.; Takats, J. *J. Am. Chem. Soc.* **1997**, *119*, 11088.

59. Grevels, F-W.; Schneider, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 410.

60. Tang, J.; Shinokubo, H.; Oshima, K. *Organometallics* **1998**, *17*, 290.

61. Schweibert, K. E.; Stryker, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 8275.

62 Schweibert, K. E. *Ph.D. Dissertation*, Indiana University, **1993**.

63. (a) Oppolzer, W. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Silkinson, G., Eds.; Elsevier: New York, 1995; Vol 12, p 905. (b) Krysan, D. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Silkinson, G., Eds.; Elsevier: New York, 1995; Vol 12, p 959.

64. Green, M.; Taylor, S. J. *J. Chem. Soc., Dalton Trans.* **1975**, *1142*.

65. (a) Heimbeck, P.; Jolly, P. W.; Wilke, G. *Adv. Organomet. Chem.* **1970**, *8*, 29. (b) Bussemeier, B.; Jolly, P. W.; Wilke, G. *J. Am. Chem. Soc.* **1974**, *96*, 4726. (c) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 186.

66. (a) Trost, B. M.; Indolese, A. *J. Am. Chem. Soc.* **1993**, *115*, 4361. (b) Ikeda, S.; Sato, Y. *J. Am. Chem. Soc.* **1994**, *116*, 5975. (c) Ikeda, S.-I.; Cui, D.-M.; Sato, Y. J. Org. Chem. 1994, 59, 6877. (d) Okada, K.; Oshima, K.; Utimoto, K. *J. Am.*

*Chem. Soc.* **1996**, *118*, 6076 and references therein. (e) Yamaguchi, M.; Sotokawa, T.; Hirama, M. *Chem. Commun.* **1997**, 743 and references therein. (f) Trost, B. M.; Portnoy, M.; Kurihara, H. *J. Am. Chem. Soc.* **1997**, *119*, 836. (g) Harayama, H.; Kuroki, T.; Kimura, M.; Tanaka, S.; Tamaru, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2352.

67. (a) Inoue, Y.; Ohuchi, K.; Kawamata, T.; Ishiyama, J.; Imaizumi, S. *Chem. Lett.* **1991**, 835.

68. Welker, M. E. *Chem. Rev.* **1992**, *92*, 97.

69. Reviews: (a) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1. (b) Jones, M. D.; Kemmitt, R. D. W. *Adv. Organomet. Chem.* **1987**, *27*, 279. (c) Trost, B. M. *Pure Appl. Chem.* **1988**, *60*, 1615. (d) Ohta, T.; Takaya, H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 1185. (e) Dzhemilev, U. M.; Khusnutdinov, R. I.; Tolstikov, G. A. *J. Organomet. Chem.* **1991**, *409*, 15.

70. (a) Binger, P.; Lu, Q-H.; Wedermann, P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 316. (b) Lewis, R. T.; Motherwell, W. B.; Shipman, M. *J. Chem. Soc., Chem. Commun.* **1988**, 948. (c) Yamago, S.; Ejiri, S.; Nakamura, E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2154. See also: (d) Trost, B. M.; Balkovec, J. M.; Angle, S. R. *Tetrahedron Lett.* **1986**, *27*, 1445. See also references 30a and 54.

71. (a) Bapuji, S. A.; Motherwell, W. B.; Shipman, M. *Tetrahedron Lett.* **1989**, *30*, 7107. (b) Lautens, M.; Ren, Y.; Delanghe, P. H. M. *J. Am. Chem. Soc.* **1994**, *116*, 8821. (c) Lautens, M.; Ren, Y. *J. Am. Chem. Soc.* **1996**, *118*, 9597.

72. (a) Semmelhack, M. *Org. React.* **1972**, *19*, 115. (b) Heimbach, P. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 975. (c) Baker, R. *Chem. Rev.* **1973**, *73*, 487. (c) Billington, D. C. *Chem. Soc. Rev.* **1985**, 93. (d) Benn, R.; Gabor, G.; Jolly, P. W.; Mynott, R.; Raspel, B. *J. Organomet. Chem.* **1985**, *296*, 443. (e) Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 1286.

73. Early reviews: (a) Chiusoli, G. P.; Cassar, L. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 124. (b) Chiusoli, G. P. *Acc. Chem. Res.* **1973**, *6*, 422.

74. (a) Camps, F.; Coll, J.; Moreto, J. M.; Torras, J. *Tetrahedron Lett.* **1985**, *26*, 6397. (b) Camps, F.; Coll, J.; Moreto, J. M.; Torras, J. *Tetrahedron Lett.* **1987**, *40*, 4745. Camps, F.; Coll, J.; Llebaria, A.; Moreto, J. M. *Tetrahedron Lett.* **1988**, *29*, 5811. (d) Camps, F.; Coll, J.; Moreto, J. M.; Torras, J. *J. Org. Chem.* **1989**, *54*, 1969. (e) Camps, F.; Llebaria, A.; Moreto, J. M.; Pages, L. *Tetrahedron Lett.* **1992**, *33*, 109. (f) Camps, F.; Llebaria, A.; Moreto, J. M.; Pages, L. *Tetrahedron Lett.* **1992**, *33*, 113. (g) Camps, F.; Moreto, J. M.; Pages, L. *Tetrahedron* **1992**, *48*, 3147. (h) Pages, L.; Llebaria, A.; Camps, F.; Molins, E.; Miravitlles, C.; Moreto, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 10449. (i) Llebaria, A.; Moreto, J. M.; *J. Organomet. Chem.* **1993**, *451*, 1. (j) Villar, J. M.; Delgado, A.; Llebaria, A.; Moreto, J. M. *Tetrahedron: Asymmetry* **1995**, *6*, 665. (k) Villar, J. M.; Delgado, A.; Llebaria, A.; Moreto, J. M.; Molins, E.; Miravitlles, C. *Tetrahedron* **1996**, *52*, 10525. (l) Vilaseca, F.; Pages, L.; Villar, J. M.; Llebaria, A.; Delgado, A.; Moreto, J. M. *J. Organomet. Chem.* **1998**, *551*, 107. (m) Garcia-Grande, G.; Moreto, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 878.

75. Oppolzer, W.; Bedoya-Zurita, M.; Switzer, C. Y. *Tetrahedron Lett.* **1988**, *29*, 6433.

76. Older, C. O.; Stryker, J. M. Manuscript in preparation.

77. Appleton, T. G.; Clark, H. C.; Poller, R. C.; Puddephatt, R. J. *J. Organometal. Chem.* **1972**, *39*, C13.

78. (a) Sbrana, G.; Braca, G.; Benedetti, E. *J. Chem. Soc., Dalton Trans.* **1975**, 755. (b) Fischer, R. A.; Herrmann, W. A. *J. Organometal. Chem.* **1989**, *377*, 275.

79. Betz, P.; Jolly, P. W.; Kruger, C.; Zakrzewski, U. *Organometallics* **1991**, *10*, 3520.

80. (a) Greco, A.; Green, M.; Stone, F. G. A. *J. Chem. Soc. (A)* **1971**, 3476. (b) Bottrill, M.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 292.

81. Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2044.

82. (a) (a) Biasotto, F.; Etienne, M.; Dahan, F. *Organometallics* **1995**, *14*, 1870. (b) Barrado, G.; Hricko, M. M.; Miguel, D.; Riera, V.; Wally, H.; Garcia-Granda, S. *Organometallics* **1998**, *17*, 820.

83. (a) Lutsenko, Z. L.; Kisin, A. V.; Kuznetsova, M. G.; Bezrukova, A. A.; Khandkarova, V. S.; Rubezhov, A. Z. *Inorg. Chim. Acta.* **1981**, *53*, L28. (b) Lutsenko, Z. L.; Kisin, A. V.; Kuznetsova, M. G.; Rubezhov, A. Z. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 1420. Engl. Translation: *Bull. Acad. Sci. USSR* **1981**, 1141. (c) Lutsenko, Z. L.; Rubezhov, A. Z. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 1412. Engl. Translation: *Bull. Acad. Sci. USSR* **1982**, 1259. (d) Lutsenko, Z. L.; Aleksandrov, G. G.; Petrovskii, P. V.; Shubina, E. S.; Andrianov, V. G.; Struchkov, Y. T.; Rubezhov, A. Z. *J. Organometal. Chem.* **1985**, *281*, 349.

84. Nehl, H. *Chem. Ber.* **1993**, *126*, 1519.

85. Nehl, H. *Chem. Ber.* **1994**, *127*, 2535.

86. Lutsenko, Z. L.; Petrovskii, P. V.; Bezrukova, A. A.; Rubezhov, A. Z. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, 855. Engl. Translation: *Bull. Acad. Sci. USSR* **1988**, 735.

87. $\eta^3$-pentadienyl iridium: (a) Bleeke, J. R.; Luaders, S. T. *Organometallics* **1995**, *14*, 1667. (b) Powell, P. *Adv. Organomet. Chem.* **1986**, *26*, 125.

88. Etkin, N.; Stryker, J. M. unpublished results.

89. Etkin, N.; Dzwiniel, T. L.; Schweibert, K. E.; Stryker, J. M.; *J. Am. Chem. Soc.* **1998**, *120*, 9702.

90. (a) Frith, S. A.; Spencer, J. L. *Inorg Synth.* **1985**, *23*, 15. (b) Nicholls, J. C.; Spencer, J. L. *Inorg. Synth.* **1990**, *28*, 278. (c) Beevor, R. G.; Frith, S. A.; Spencer, J. L. *J. Organomet. Chem.* **1981**, *221*, C25. For $C_5Me_4Et$ analogue, see: (d) Green, M. L. H.; Pardy, R. B .A. *J. Chem. Soc., Dalton Trans.* **1979**, 355.

91. Schwiebert, K. E.; Stryker, J. M. *Organometallics* **1993**, *12*, 600.

92. (a) Rosan, A. M. *J. Chem. Soc., Chem. Commun.* **1981**, 311. (b) Rosan, A. M.; Romano, D. M. *Organometallics* **1990**, *9*, 1048. See also: (c) Ito, T.; Yoden, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2365. (d) Krivykh, V. V.; Gusev, O. V.; Rybinskaya, M. I. *Izv. Akad. Nauk SSSR* **1983**, 1178. English Translation: *Bull. Acad. Sci. USSR* **1983**, 1081.

93. (a) Fischer, E. O.; Fischer, R. D. *Z. Naturforsch.* **1961**, *16B*, 475. (b) Heck, R. F. *J. Org. Chem.* **1963**, *28*, 604. (c) Heck, R. F. *Inorg. Chem.* **1965**, *4*, 855. (d) Aviles, T.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1116. (e) Aviles, T.; Barroso, F.; Royo, P.; Noordik, J. H. *J. Organomet. Chem.* **1982**, *236*, 101. (f) Aviles, T.; Barroso, F.; Royo, P. *J. Organomet. Chem.* **1987**, *326*, 423. (g) Lehmkuhl, H.; Nehl, H. F. *Chem. Ber.* **1984**, *117*, 3443. See also reference 83.

94. King, J. A., Jr.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1993**, *460*, 91. See also reference 92d.

95. (a) King, R. B.; Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3593. (b) Herrmann, W. A.; Huggins, J. M.; Reiter, B.; Bauer, C. *J. Organomet. Chem.* **1981**, *212*, C19. (c) Dudeney, N.; Green, J. C.; Kirchner, O. N.; Smallwood, F. St. J. *J. Chem. Soc., Dalton Trans.* **1984**, 1883. (d) tom Dieck, H.; Haarich, M. *J. Organomet. Chem.* **1985**, *291*, 71. (e) Olson, W. L.; Nagaki, D. A.; Dahl, L. F. *Organometallics* **1986**, *5*, 630. (f) Carl, R. T.; Doig, S. J.; Geiger, W. E.; Hemond, R. C.; Hughes, R. P.; Kelly, R. S.; Samkoff, D. E. *Organometallics* **1987**, *6*, 611. (g) Kaganovich, V. S.; Kudinov, A. R.; Rybinskaya, M. I. *J. Organomet. Chem.* **1987**, *323*, 111. (h) Hill, R. H. *J. Chem.*

*Soc., Chem. Commun.* **1989**, *293* and references therein. (i) Kato, A.; Tono, M.; Hisamatsu, N.; Nozawa, S.; Sugiyama, T.; Kajitani, M.; Akiyama, T.; Sugimori, A. *Chem. Lett.* **1992**, 243. (j) Kato, A.; Tono, M.; Hisamatsu, N.; Nozawa, S.; Ninomiya, K.; Sugiyama, T.; Kajitani, M.; Akiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1994**, *473*, 313.

96. Beevor, R. G.; Frith, S. A.; Spencer, J. L. *J. Organomet. Chem.* **1981**, *221*, C25.

97. Brandsma, L.; Verkruijsse, H. D. *Synthesis*, **1978**, 290.

98. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5th Ed. John Wiley and Sons, Inc., **1991**.

99. Pearson, A. J.; Kole, S. L.; Chen, B. *J. Am. Chem. Soc.* **1983**, *105*, 4483. (b) Pearson, A. J.; Kole, S. L.; Ray, T. *J. Am. Chem. Soc.* **1984**, *106*, 6060.

100. (a) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. (C)* **1969**, 2024. (b) Szajek, L. P.; Shapley, J. R. *Organometallics*, **1991**, *10*, 2512 and refereneces therein.

101. Kaneda, K.; Uchiyama, T.; Fujiwara, Y.; Imanaka, T.; Teranishi, S. *J. Org. Chem.* **1979**, *44*, 55.

102. Shapiro reaction reviews: (a) Shapiro, R. H. *Org. React.* **1975**, *23*, 405. (b) Adlington, R. M.; Barrett, A. G. M. *Acc. Chem. Res.* **1983**, *16*, 55.

103. Cp*$CoCl_2$ dimer: (a) Koelle, U.; Fuss, B. *Chem. Ber.* **1984**, *117*, 743. (b) Koelle, U.; Fuss, B. *Chem. Ber.* **1984**, *117*, 753. (c) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698. For the analogous Cp*$CoI_2$ dimer see: (d) Roie, D. M.; Maitlis, P. M. *J. Chem. Soc. (A)* **1971**, 3173.

104. *Organometallics in Synthesis. A Manual.* Schlosser, M., Ed. John Wiley and Sons, Inc. New York, 1994.

105. Cp*$CoI_2(CO)$: King, R. B.; Efrety, A.; Douglas, W. M. J. Organomet. Chem. 1973, 56, 345.

106. (a) Koelle, U.; Khouzami, F.; Fuss, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 131. Koelle, U.; Khouzami, F.; Fuss, B. *Angew. Chem. Suppl.* **1982**, 230. (b) Koelle, U.; Fuss, B.; Belting, M.; Raabe, E. *Organometallics* **1986**, *5*, 980.

107. Alkoxyacetylenes: (a) Jones, E. R. H.; Eglinton, G.; Whiting, M. C.; Shaw, B. L. *Org. Synth. Coll. Vol. IV* **1963**, 404. (b) Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1980**, *102*, 5253. (c) Pericas, M. A.; Serratosa, F.; Valenti, E. *Tetrahedron* **1987**, *43*, 2311. (d) Stalick, W. M.; Hazlett, R. N.; Morris, R. E. *Synthesis* **1988**, 287 and references therein.

108. (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474. (c) Watasuki, Y.; Koga, N.; Werner, H.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 360 and references therein.

109. Wadepohl, H.; Galm, W.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 686.

110. Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R., Ed. *Vogel's Textbook of Practival Organic Chemistry*, 5th Ed. John Wiley and Sons: New York, 1989.

111. Cope, A. C.; Ciganek, E. *Org. Syn. Coll. Vol. 4*, **1963**, 612.

112. Cyclopentenecarbaldehyde: Brown, J. B.; Henbest, H. B.; Jones, E. R. H. *J. Chem. Soc.* **1950**, 3634.

113. (a) Pal, P. R.; Skinner, C. G.; Dennis, R. L.; Shive, W. *J. Am. Chem. Soc.* **1956**, *78*, 5116. (b) Roustan, J. L.; Merour, J. Y.; Charrier, C.; Benaim, J.; Cadiot, P. *J. Organometal. Chem.* **1979**, *168*, 61. For preparation of the corresponding chloro compound see: (c) Bullivant, M. J.; Pattenden, G. *J. Chem. Soc. Perkin Trans. (I)* **1976**, 249. (d) Ho, P.-T.; Kolt, R. J. *Can. J. Chem.* **1982**, *60*, 663.

114. (a) Kirihara, M.; Kambayashi, T.; Momose, T. *Chem. Commun.* **1996**, 1103. (b) Song, Z.; Beak, P. *J. Am. Chem. Soc.* **1990**, *112*, 8126. (c) Shea, K. J.; Stoddard, G. J.; England, W. P.; Haffner, C. D. *J. Am. Chem. Soc.* **1992**, *114*, 2635.

115. The numbering schemes for the crystallographic assignments may or may not match those presented for the spectroscopic data. Non-hydrogen atoms are represented by Gaussian ellopsoids at the 20% probability level. Hydrogen atoms are not located, but are shown with arbitrarily small thermal parameters. All data was collected at -60°C.

116. Prepared from cyclopentanone, vinyl Grignard, then $H_2SO_4$-catalyzed dehydration. 1-Vinylcyclopentene has been prepared using a different methodology. See: (a) Meier, H.; Schmitt, M. *Tetrahedron Lett.* **1989**, *30*, 5873. (b) Stierman, T. J.; Johnson, R.P. *J. Am. Chem. Soc.* **1985**, *107*, 3971.

117. $CpCo(C_2H_4)_2$: (a) Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 716. (b) Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem. Suppl.* **1983**, 1005. (c) Jonas, K.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 520. (d) Jonas, K. *Adv. Organomet. Chem.* **1981**, *19*, 97. (e) Jonas, K. *Pure Appl. Chem.* **1984**, *56*, 63. (f) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295. See also: (g) Benn, R.; Cibura, K.; Hofmann, P.; Jonas, K.; Rufinska, A. *Organometallics* **1985**, *4*, 2214. For the analogous iron complexes, see: (h) Jonas, K.; Schieferstein, L *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 549. For the reaction with allyl bromide, see reference 92f.

118. $CpCo(cycloheptadienyl)^+$: (a) Salzer, A.; Bigler, P. *Inorg. Chim. Acta* **1981**, *48*, 199. CpCo(cycloheptatriene): (b) Benn, R.; Cibura, K.; Hofmann, P.; Jonas, K.; Rufinska, A. *Organometallics* **1985**, *4*, 2214. See also references 117 and 118a.

119. Evans, J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 510.

120. Older, C. M.; Stryker, J. M. *Unpublished results.*

121. (a) Bleeke, J. R.; Peng, W. *Organometallics* **1987**, *6*, 1576. (b) Bleeke, J. R.; Peng, W.; Xie, Y.; Chiang, M. Y. *Organometallics* **1990**, *9*, 1113.

122. (a) Egan, J. W., Jr.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1578. (b) Donovan, B.T.; Hughes, R. P.; Trujillo, H. A. *J. Am. Chem. Soc.* **1990**, *112*, 7076.

123. (a) Dubeck, M.; Filbey, A. H. *J. Am. Chem. Soc.* **1961**, *83*, 1257. (b) Wilke, G.; Bogdanovic, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kroner, M.; Oberkirch, W.; Tanaka, K.; Walter, D.; Zimmermann, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 151. ($C_5H_5$)(cyclopentenyl)Ni has been made using other methodology: (c) Lehmkuhl, H.; Rufinska, A.; Naydowski, C.; Mynott, R. *Chem. Ber.* **1984**, *117*, 376.

124. (a) Lee, H-B.; Mosely, K.; White, C.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1975**, 2322

125. Mosely, K.; Kang, J. W.; Maitlis, P. M. *J. Chem. Soc. (A)* **1970**, 2875.

126. (a) Oldham, W. J., Jr.; Hinkle, A. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 11028. (b) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913 and references therein. (c) Duckett, S. B.; Haddleton, D. M.; Jackson, S. A.; Perutz, R. N.; Poliakoff, M.; Upmacis, R. K. *Organometallics* **1988**, *7*, 1526.

127. Leonova, E. V.; Malkov, A. V.; Kochetkova, N. O.; Sokolova, A. N.; Rukhlyada, N. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 728. Engl. Translation: *Bull. Acad. Sci. USSR* **1984**, 678.

128. (a) Bennett, M. A.; Nicholls, J. C.; Rahman, A. K. F.; Redhouse, A. D.; Spencer, J. L.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1328. (b) Nicholls, J. C.; Spencer, J. L. *Organometallics* **1994**, *13*, 1781. (c) Cracknell, R. B.; Nicholls, J. C.; Spencer, J. L. *Organometallics* **1996**, *15*, 446.

129. (a) Lewis, J.; Parkins, A. W. *J. Chem. Soc. (A)* **1967**, 1150. (b) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 1305. (c)

Bouachir, F.; Chaudret, B.; Neibecker, D.; Tkatchenko, I. *Angew. Chem., Int. Ed. Engl.* **1985**, *4*, 347. (c) Bouachir, F.; Chaudret, B.; Tkatchemko, I. *J. Chem. Soc., Chem. Commun.* **1986**, 94. (d) Ashworth, T. V.; Chalmers, A. A.; Liles, D. C.; Meintjies, E.; Singleton, E. *Organometallics* **1987**, *6*, 1543. (e) Bouachir, F.; Chaudret, B.; Dahan, F.; Agbossou, F.; Tkatchenko, I. *Organometallics* **1991**, *10*, 455. For an example of a seven-membered ring with an allyl-olefin structure, see (f) Lewis, J.; Parkins, A. W. *J. Chem. Soc. (A)* **1969**, 953.

130. Chen, J.-X.; Stryker, J. M. *Unpublished results.*

131. Bulsara, J.; Stryker, J. M. *Unpublished results.*

132. Reviews: (a) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, 34, 3047. (b) Pearson, A. J. *Pure Appl. Chem.* **1983**, *55*, 1767. (c) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. W. *Chem. Rev.* **1984**, *84*, 525. (d) Pearson, A. J. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 4, p 663. (e) Pearson, A. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Silkinson, G., Eds.; Elsevier: New York, 1995; Vol 12, p 637.

133. (a) Kane-Maguire, L. A. P.; Mouncher, P. A.; Salzer, A. *J. Organometal. Chem.* **1979**, *168*, C42. (b) Kane-Maguire, L. A. P.; Mouncher, P. A.; Salzer, A. *J. Organometal. Chem.* **1988**, *347*, 383.

134. Wieser, M.; Karaghiosoff, K.; Beck, W. *Chem. Ber.* **1993**, *126*, 1081.

135. Huffer, S.; Wieser, M.; Polborn, K.; Sunkel, K.; Beck, W. *Chem. Ber.* **1994**, *127*, 1369.

136. Geiger, W. E.; Gennett, T.; Lane, G. A.; Salzer, A.; Rheingold, A. L. *Organometallics* **1986**, *5*, 1352. (b) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189 and references therein. (c) Gaudet, M. V.; Hanson, A. W.; White, P. S.; Zaworotko, M. J. *Organometallics* **1989**, *8*, 286. (d) Lehmann, R. E.; Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 458. (e) Aggerwal, R. P.; Connelly, N.

G.; Dunne, B. J.; Gilbert, M.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 1. (f) Lehmann, R. E.; Kochi, J. K. *Organometallics* **1991**, *10*, 190. (g) Niemer, B.; Breimair, J.; Wagner, B.; Polborn, K.; Beck, W. *Chem. Ber.* **1991**, *124*, 2227. (h) Thompson, R. L.; Gieb, S. J.; Cooper, N. J. *J. Am. Chem. Soc.* **1991**, *113*, 8961. (i) Lee, S.; Lovelace, S. R.; Arford, D. J.; Geib, S. J.; Weber, S. G.; Cooper, N. J. *J. Am. Chem. Soc.* **1996**, *118*, 4190. (j) Sun, S.; Dullaghan, C. A.; Sweigart, D. A. *J. Chem. Soc., Dalton Trans.* **1996**, 4493. (k) Hsu, S. C. N.; Yeh, W.-Y.; Lee, G.-H.; Peng, S.-M. *J. Am. Chem. Soc.* **1998**, *120*, 13250. See also reference 130b.

137. $\eta^4$-diene structures: (a) Erker, G.; Kruger, C.; Muller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1. (b) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120.

138. (a) Wakatsuki, Y.; Yamazaki, H. *J. Organometal. Chem.* **1977**, *139*, 169. (b) Nicholas, K. M.; Pettit, R. *Tetrahedron Lett.* **1971**, *37*, 3475. (c) Gesing, E. R. F.; Tane, J. P.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1023. (d) Tane, J. P.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed.* Engl. **1982**, *21*, 617. (e) Saha, M.; Nicholas, K. M. *J. Org. Chem.* **1984**, *49*, 417. (f) Grotjahn, D. B.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 2091. (g) Grotjahn, D. B.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1990**, *112*, 5653. (h) Johnson, E. P.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1991**, *113*, 381. (i) Gleiter, R.; Merger, R.; Nuber, B. *J. Am. Chem. Soc.* **1992**, *114*, 8921. (j) Boese, R.; Van Sickle, A. P., Vollhardt, K. P. C. *Synthesis* **1994**, 1374. (k) Jiang, S.; Turos, E. *Tetrahedron Lett.* **1994**, *35*, 7889. (l) Franck-Neumann, M.; Geoffrey, P. *Tetrahedron Lett.* **1994**, *35*, 7027. (m) Tanaka, S.; Isobe, M. *Synthesis* **1995**, 859. (n) Feiken, N.; Schreuder, P.; Siebenlist, R.; Fruhauf, H.-W.; Vrieze, K.; Kooijman, H.; Veldman, N.; Spek, A. L.; Fraanje, J.; Goubitz, K. *Organometallics* **1996**, *15*, 2148. (o) Taya, K.; Nagasawa, T.; Suzuki, K. *Synlett* **1997**, 304. (p) Bohmer, J.;

Hampel, F.; Schobert, R. *Synthesis*, **1997**, 661. (q) Franck-Neumann, M.; Bissinger, P.; Geoffroy, P. *Tetrahedron Lett.* **1997**, *38*, 4477.

139. Fairhurst, C.; White, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1524.

140. (a) Wender, P. A.; Lee, H. Y.; Wilhelm, R. S.; Williams, P. D. *J. Am. Chem. Soc.* **1989**, *111*, 8954 and references therein. (b) Wender, P. A.; Kogen, H.; Lee, H. Y.; Munger, J. D., Jr.; Wilhelm, R. S.; Williams, P. D. *J. Am. Chem. Soc.* **1989**, *111*, 8957. See also reference 25.

141. (a) Tjaden, E. B.; Casty, G. L.; Stryker, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 9814. (b) Casty, G. L.; Stryker, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 7814 and references therein. (c) Carter, C. A. G.; McDonald, R.; Stryker, J. M. *Organometallics*, **1999**, *18*, 820. (d) Carter, C. A. G. *Ph.D. Dissertation*, University of Alberta, **1998**.

142. (a) Crabtree, R. H. *Chem. Rev.* **1985**, 85, 245. (b) Merola, J. S. *Curr. Org. Chem.* **1997**, *1*, 235.

143. (a) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987. (b) Schneider, J. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1068. (c) Lohrenz, J. C. W.; Jacobsen, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1305. (d) Herrmann, W. A.; Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1049. (e) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879 and references therein. See also: Buchmann, B.; Piantini, U.; von Phillipsborn, W.; Salzer, A. *Helv. Chim. Acta* **1987**, *70*, 1487.

144. Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, 106, 7272. Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, 108, 7346 and references therein.

145. Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1973**, 12, 173.

146. (a) Hourliet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818. (b) Armentrout, P. B.; Beauchamp, J. L. *Acc. Chem. Res.* **1989**, *22*, 315. (c) Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121. (d) Schwartz, H. *Acc. Chem. Res.* **1989**, *22*, 282. (e) Hornung, G.; Schroder, D.; Schwarz, H. *J. Am. Chem.*

*Soc.* **1997**, *119*, 2273. (f) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360. (g) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565. (h) van Koppen, P. A. M.; Bowers, M. T.; Haynes, C. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1998**, *120*, 5704 and references therein.

147. Halpern, J. *Acc. Chem. Res.* **1982**, 15, 238.

148. Mondal, J. U.; Blake, D. M. *Coord. Chem. Rev.* **1982**, *47*, 205.

149. (a) Tipper, C. F. H. *J. Chem. Soc.* **1955**, 2045. (b) Adams, D. M.; Chatt, J.; Guy, R. G.; Sheppard, N. *J. Chem. Soc.* **1961**, 738. (c) Bailey, N. A.; Gillard, R. D.; Keeton, M.; Mason, R.; Russell, D. R. *Chem. Comm.* **1966**, 396. (d) Roundhill, D. M.; Lawson, D. N.; Wilkinson, G. *J. Chem. Soc. (A)* **1968**, 845. (e) Noyori, R.; Takaya, H. *Chem. Comm.* **1969**, 525. (f) Binns, S. E.; Cragg, R. H.; Gillard, R. D.; Heaton, B. T.; Pilbrow, N. F. *J. Chem. Soc. (A)* **1969**, 1227.

150. (a) Bishop, K. C., III *Chem. Rev.* **1976**, *76*, 461. (b) Puddephatt, R. *J. Coord. Chem. Rev.* **1980**, *33*, 149. (c) Wong, H. N. C.; Hon, M.-Y.; Tse, C.-W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165. (d) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241. Recent examples of three-membered ring interaction with metal complexes: (e) Li, R. T.; Nguyen, S. T.; Grubbs, R. H.; Ziler, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 10032. (f) Jun, C.-H.; Kang, J.-B.; Lim, Y.-G. *Tetrahedron Lett.* **1995**, *36*, 277. (g) Foerstner, J.; Kakoschke, A.; Stellfeldt, D.; Butenschon, H.; Wartchow, R. *Organometallics* **1998**, *17*, 893. (h) Osakada, K.; Takimoto, H.; Yamamoto, T. *Organometallics* **1998**, *17*, 4532 and references therein.

151. Recent examples: (a) Inoue, Y.; Hibi, T.; Satake, M.; Hashimoto, H. *J. Chem. Soc., Chem. Comm.* **1979**, 982. (b) Aoki, S.; Fujimura, T.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1988**, *110*, 3296. (c) Fujimura, T.; Aoki, S.; Nakamura, E. *J. Org. Chem.* **1991**, *56*, 2809. (d) Bessmertnykh, A. G.; Blinov, K. A.; Grishin, Y. K.; Donskaya, N. A.; Beletskaya, I. P. *Tetrahedron Lett.* **1995**, *36*,

7901. (e) Tsukada, N.; Shibuya, A.; Nakamura, I.; Yoshinori, Y. *J. Am. Chem. Soc.* **1997**, *119*, 8123. Ring opening followed by polymerization: (f) Jia, L.; Yang, X.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 1547 and references therein. Insertion of CO into cyclopropenium ligands: (g) Green, M.; Hughes, R. P. *J. Chem. Soc., Chem. Comm.* **1975**, 862. (h) Donaldson, W. A.; Hughes, R. P.; *J. Am. Chem. Soc.* **1982**, *104*, 4846. (i) Henry, W. P.; Hughes, R. P. *J. Am. Chem. Soc.* **1986**, *108*, 7862.

152. Wick, D. D.; Northcutt, T. O.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4484.

153. (a) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795. (b) Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076. (c) Ermer, S. P.; Struck, G. E.; Bitler, S. P.; Richards, R.; Bau, R.; Flood, T. C. *Organometallics* **1993**, *12*, 2634.

154. Bond, A.; Bottrill, M.; Green, M.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1977**, 2372.

155. Murakami, M.; Takahashi, K.; Amii, H.; Ito, Y. *J. Am. Chem. Soc.* **1997**, *119*, 9307.

156. Jun, C.-H. *Organometallics* **1996**, *15*, 895.

157. Adams, R. D.; Chen, L.; Qu, X. *Organometallics* **1994**, *13*, 1992.

158. Atkinson, E. R.; Levins, P. L.; Dickelman, T. E. *Chem. Ind. (London)* **1964**, 934.

159. (a) Lu, Z.; Jun, C.-H.; de Gala, S.; Sigalas, M.; Eisenstein, O.; Crabtree, R. H. *J. Chem. Soc., Chem. Comm.* **1993**, 1877. (b) Lu, Z.; Jun, C.-H.; de Gala, S.; Sigala, M. P.; Eisenstein, O.; Crabtree, R. H. *Organometallics* **1995**, *14*, 1168. (c) Perthuisot, C.; Edelbach, B. L.; Zubris, D. L.; Jones, W. D. *Organometallics* **1997**, *16*, 2016.

160. Yeh, W.-Y.; Hsu, S. C. N.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1998**, *17*, 2477.

161. Eisch, J. J.; Piotrowski, A. M.; Han, K. I.; Kruger, C.; Tsay, Y. H. *Organometallics* **1985**, *4*, 224. See also reference 155.

162. (a) Perthuisot, C.; Jones, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 3647. (b) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843. (c) Edelbach, B. L.; Vicic, D. A.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4784.

163. Schwager, H.; Spyroudis, S.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1990**, *382*, 191.

164. (a) South, M. S.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1984**, *106*, 4181. (b) Liebeskind, L. S.; Leeds, J. P.; Baysdon, S. L.; Iyer, S. *J. Am. Chem. Soc.* **1984**, *106*, 6451. (c) Liebeskind, L. S.; Baysdon, S. L.; South, M. S.; Iyer, S.; Leeds, J. P. *Tetrahedron* **1985**, *41*, 5839. (d) Liebeskind, L. S.; Mitchell, D.; Foster, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 7908. (e) Leibeskind, L. S. *Tetrahedron* **1989**, *45*, 3053. (f) Huffman, M. A.; Liebeskind, L. S.; Pennington, W. T., Jr. *Organometallics* **1990**, *9*, 2194. (g) Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1991**, *113*, 2771.

165. (a) Evans, J. A.; Everitt, G. F.; Kemmitt, R. D. W.; Russell, D. R. *J. Chem. Soc., Chem. Comm.* **1973**, 158. (b) Hoberg, H.; Herrera, A. *Angew. Chem.,Int. Ed. Eng* **1981**, *20*, 876.

166. (a) Murakami, M.; Amii, H.; Ito, Y. *Nature* **1994**, *370*, 540. (b) Murakami, M.; Amii, H.; Shigeto, K.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 8285. (c) Murakami, M.; Itahashi, T.; Amii, H.; Takahashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9949. See also: (d) Nishimura, T.; Ohe, K.; Uemura, S. *J. Am. Chem. Soc.* **1999**, *121*, 2645 and references therein.

167. (a) Muller, E.; Segnitz, A.; Langer, E. *Tetrahedron Lett.* **1969**, *14*, 1129. (b) Kaneda, K.; Azuma, H.; Wayaku, M.; Teranishi, S. *Chem. Lett.* **1974**, 215.

168. (a) Kang, J. W.; Maitlis, P. M. *J. Am. Chem. Soc.* **1968**, *90*, 3259. (b) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

169. (a) King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1972**, *94*, 3773. (b) King, R. B.; Douglas, W. M.; Efraty, A. *J. Organomet. Chem.* **1974**, *69*, 131.

170. (a) Eilbracht, P. *Chem. Ber.* **1976**, *109*, 1429. (b) Eilbracht, P. *Chem. Ber.* **1976**, *109*, 3136. (c) Eilbracht, P. *J. Organomet. Chem.* **1976**, *120*, C37. (d) Eilbracht, P.; Dahler, P. *J. Organomet. Chem.* **1977**, *127*, C48. (e) Eilbracht, P.; Mayser, U. *J. Organomet. Chem.* **1977**, *135*, C26. (f) Eilbracht, P.; Dahler, P. *J. Organomet. Chem.* **1977**, *125*, C23. (g) Eilbracht, P.; Dahler, P. *Chem. Ber.* **1980**, *113*, 542. (h) Eilbracht, P.; Dahler, P.; Mayser, U.; Henkes, E. *Chem. Ber.* **1980**, *113*, 1033. (i) Eilbracht, P.; Mayser, U. *Chem. Ber.* **1980**, *113*, 2211. (j) Eilbracht, P.; Mayser, U.; Tiedtke, G. *Chem. Ber.* **1980**, *113*, 1420.

171. (a) Barretta, A.; Cloke, F. G., N.; Feigenbaum, A.; Green, M. L. H., Gourdon, A.; Prout, K. *J. Chem. Soc., Chem. Comm.* **1981**, 156. (b) Baretta, A.; Chong, K. S.; Cloke, F. G. N.; Feigenbaum, A.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1983**, 861.

172. Gladyz, J. A.; Fulcher, J. G.; Ugolick, R. C.; Hanlan, A. J. L.; Bocarsly, A. B. *J. Am. Chem. Soc.* **1979**, *101*, 3388. (b) Green, M. L. H.; Wong, L.-L. *J. Chem. Soc., Chem. Comm.* **1984**, 1442. (c) Fu, Y.-T.; Chao, P.-C.; Liu, L.-K. *Organometallics* **1998**, *17*, 221.

173. (a) Crabtree, R. H.; Dion, R. P. *J. Chem. Soc., Chem. Comm.* **1984**, 1260. (b) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222. (c) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324.

174. (a) Jones, W. D.; Maguire, J. A. *Organometallics* **1987**, *6*, 1301. (b) Hemond, R. C.; Hughes, R. P.; Locker, H. B. *Organometallics* **1986**, *5*, 2391.

175. (a) DiMauro, P. T.; Wolczanski, P. T. *Organometallics* **1987**, *6*, 1947. (b) DiMauro, P. T.; Wolczanski, P. T.; Parkanyi, L.; Petach, H. H. *Organometallics* **1990**, *9*, 1097. (c) DiMauro, P. T.; Wolczanski, P. T. *Polyhedron* **1995**, *14*, 149. (d) Hoffmann, R.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *82*, 598.

176. (a) Rondon, D.; Chaudret, B.; He, X.-D.; Labroue, D. *J. Am. Chem. Soc.* **1991**, *113*, 5671. (b) Halcrow, M. A.; Urbanos, F.; Chaudret, B. *Organometallics* **1993**, *12*, 955. (c) Urbanos, F.; Halcrow, M. A.; Fernadez-Baeza, J.; Dahan, F.; Labroue, D.; Chaudret, B. *J. Am. Chem. Soc.* **1993**, *115*, 3484. (d) Chaudret, N. *Bull. Soc. Chim. Fr.* **1995**, *132*, 268. (e) Masuda, K.; Ohkita, H.; Kurumatani, S.; Itoh, K. *Organometallics* **1993**, *12*, 2221.

177. Older, C. M.; Stryker, J. M. *Organometallics* **1998**, *17*, 5596.

178. (a) Roman, E.; Astruc, D. *Inorg. Chim. Acta.* **1979**, *37*, L465. (b) Astruc, D. *Tetrahedron* **1983**, *39*, 4027. See also: (c) Fischer, E. O.; Elschenbroich, C. *Chem. Ber.* **1970**, *103*, 162.

179. (a) Suggs, J. W.; Cox, S. D. *J. Organomet. Chem.* **1981**, *221*, 199. (b) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1984**, *106*, 3054. (c) Suggs, J. W.; Wovkulich, M. J.; Cox, S. D. *Organometallics* **1985**, *4*, 1101. (d) Suggs, J. W.; Jun, C.-H. *J. Chem. Soc., Chem. Comm.* **1985**, 92. (e) Suggs, J. W.; Movkulich, M. J.; Lee, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 5546. (f) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1986**, *108*, 4679. (g) Jun, C.-H.; Lee, H. *J. Am. Chem. Soc.* **1999**, *121*, 880.

180. (a) Terheijden, J.; van Koten, G.; Vinke, I. C.; Spek, A. L. J. *Am. Chem. Soc.* **1985**, *107*, 2891. (b) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699. (c) Jones, W. D. *Nature* **1993**, *364*, 676. (d) Gozin, M.; Aizenberg, M.; Liou, S.-Y.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1994**, *370*, 42. (e) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 9774. (f) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Chem. Soc., Chem. Comm.* **1995**, 1965. (g) van der Boom, M. E.; Kraatz, H.-B.; Ben-David, Y.; Milstein, D.

*J. Chem. Soc., Chem. Comm.* **1996**, 2167. (h) Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406. (i) Gandelman, M.; Vigalok, A.; Shimon, L. J. W.; Milstein, D. *Organometallics* **1997**, *16*, 3981. (j) Liou, S.-Y.; van der Boom, M. E.; Milstein, D. *Chem. Comm.* **1998**, 687. (k) van der Boom, M. E.; Ben-David, Y.; Milstein, D. *Chem. Comm.* **1998**, 917. (l) van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 13415. (m) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed. Eng.* **1999**, *38*, 870. (n) Rybtchinski, B; Milstein, D. *J. Am. Chem. Soc.* **1999**, *121*, 4528.

181. (a) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471. (b) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6471. (c) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51.

182. (a) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976. (b) Bercaw, J. E. *Pure Appl. Chem.* **1990**, *62*, 1151. (c) Burger, B. J.; Thompson, M.; Cotter, D.; Bercaw, J. *J. Am. Chem. Soc.* **1990**, *112*, 1566.

183. Miller, R. G.; Pinke, P. A.; Stauffer, R. D.; Golden, H. J.; Baker, D. J. *J. Am. Chem. Soc.* **1974**, *96*, 4211, 4221, 4229, 4235.

184. (a) Thompson, S. K.; Young, G. B. *Organometallics* **1989**, *8*, 2068. (b) Ankianiec, B. C.; Christou, V.; Hardy, D. T.; Thomson, S. K.; Young, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 9963.

185. Thomas, B. J.; Noh, S. K.; Schulte, G. K.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 893.

186. (a) Eshuis, J.; Tan, Y.; Teuben, J. *J. Mol. Catal.* **1990**, *62*, 277. (b) Mise, T.; Kageyama, A.; Miya, S.; Yamazaki, H. *Chem. Lett.* **1991**, 1525. (c) Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H.; Renkema, J.; Evens, G. G. *Organometallics* **1992**, *11*, 362. (d) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025. (e) Kesti, M. R.;

Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 3565. (f) Guo, Z.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424. (g) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

187. Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147.

188. Yang, X.; Jia, L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3392.

189. ROMP see: (a) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon: London, 1982; Vol. 8, p 502. See also reference 187 and references therein. Alkyne metathesis has recently been reviewed. See: (b) Bunz, U. H. F.; Kloppenburg, L. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 478 and references therein.

190. (a) McNeill, K.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 3625. (b) McNeill, K.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 11244.

191. Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1991**, *10*, 3344.

192. Horton, A. D. *Organometallics* **1996**, *15*, 2675.

193. Etienne, M.; Mathieu, R.; Donnadieu, B. *J. Am. Chem. Soc.* **1997**, *119*, 3218.

194. (a) Kondo, T.; Kodoi, K.; Nishinaga, E.; Okada, T.; Morisaki, Y.; Watanabe, Y.; Mitsudo, T. *J. Am. Chem. Soc.* **1998**, *120*, 5587. (b) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, A. M.; Onate, E.; Oro, L. A.; Tolosa, J. I. *Organometallics* **1997**, *16*, 1316.

195. (a) Grubbs, R. H.; Miyashita, A.; Liu, M.-I. M.; Burk, P. L. *J. Am. Chem. Soc.* **1977**, *99*, 3863. (b) Grubbs, R. H.; Miyashita, A. *J. Chem. Soc., Chem. Comm.* **1977**, 864. (c) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 1301. (d) Grubbs, R. H.; Miyashita, A.; Liu, M.; Burk, P. *J. Am. Chem. Soc.* **1978**, *100*, 2418. (e) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7418.

196. (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521. (b) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529.

197. Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136.

198. Diversi, P.; Ingrosso, G.; Lucherini, A. *J. Chem. Soc., Chem. Comm.* **1977**, 52.

199. (a) Erker, G.; Czisch, P.; Kruger, C.; Wallis, J. M. *Organometallics* **1985**, *4*, 2059. (b) Erker, G.; Dorf, U.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2059.

200. (a) Takahashi, T.; Tamura, M.; Saburi, M.; Uchida, Y.; Negishi, E.-I. *J. Chem. Soc., Chem. Comm.* **1989**, 852. See also: (b) Suzuki, N.; Kondakov, D. Y.; Takahashi, T. *J. Am. Chem. Soc.* **1993**, *115*, 8485.

201. Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701.

202. Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006.

203. (a) Edwin, J.; Geiger, W. E.; Salzer, A.; Ruppli, U.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 7893. (b) Geiger, W. E. ; Salzer, A.; Edwin, J.; von Philipsborn, W.; Piantini, U.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7113. (c) Evans, W. J.; Keyer, R. A.; Rabe, G. W.; Drummond, D. K.; Ziller, J. W. *Organometallics* **1993**, *115*, 9850. (d) Gallo, E.; Solari, E.; De Angelis, S.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1993**, *115*, 9850.

204. Grigsby, W. J.; Power, P. *Chem. Eur. J.* **1997**, *3*, 368.

205. (a) Klein, H.-F.; Auer, E.; Jung, T.; Rohr, C. *Organometallics* **1995**, *14*, 2725. (b) Poignant, G.; Sinbandhit, S.; Toupet, L.; Guerchais, V. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 963.

206. (a) Chiang, H.-J.; Liu, C.-S. *J. Organomet. Chem.* **1993**, *458*, 167. (b) Mitsudo, T.; Zhang, S.-W.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 435. (c) Mitsudo, T.; Suzuki, T.; Zhang, S.-W.; Imai, D.; Fujita, K.; Manabe, T.; Shiotsuki, M.; Watanabe, Y.; Wada, K.; Kondo, T. *J. Am. Chem. Soc.* **1999**, *121*,

1839 and references therein. (d) Shaltout, R. M.; Sygula, R.; Sygula, A.; Fronczek, F. R.; Stanley, G. G.; Rabideau, P. W. *J. Am. Chem. Soc.* **1998**, *120*, 835. (e) Jia, G.; Ng, W. S.; Lau, C. P. *Organometallics* **1998**, *17*, 4538.

207. (a) Pellny, P.-M.; Peulecke, N.; Burlakov, V. V.; Tillack, A.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2615. (b) Pulst, S.; Kirchbauer, F. G.; Heller, B.; Baumann, W.; Rosenthal, U. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1925 and references therein. (c) Akita, M.; Sakurai, A.; Moro-oka, Y. *Chem. Commun.* **1999**, 101 and references therein.

208. (a) Bianchini, C.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Organometallics* **1995**, *14*, 3152. (b) Bianchini, C.; Casares, J. A.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *J. Am. Chem. Soc.* **1996**, *118*, 4585. For a more general discussion of alkyne hydration to carbonyl compounds, see: (c) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley, New York, 1992; pp. 762 and other citations in reference 208b.

209. (a) Brooks, C. D.; Huang, L.; McCarron, M.; Johnstone, R. A. W. Chem. Commun. 1999, 37. For a general discussion on olefin oxidation to carbonyl compounds, see: (b) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley, New York, 1992; pp. 1177.

210. (a) Lin, M.; Hogan, T. E.; Sen, A. *J. Am. Chem. Soc.* **1996**, *118*, 4574. (c) Lin, M.; Hogan, T.; Sen, A. *J. Am. Chem. Soc.* **1997**, *119*, 6048. (d) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550.

211. (a) Suzuki, H.; Takaya, Y.; Takemori, T. *J. Am. Chem. Soc.* **1994**, *116*, 10779. (b) Takemori, T.; Suzuki, H.; Tanaka, M. *Organometallics* **1996**, *15*, 4346. (c) Matsubara, K.; Okamura, R.; Tanak, M.; Suzuki, H. *J. Am. Chem. Soc.* **1998**, *120*, 1108.

212. Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 6182.

213. (a) Lecuyer, C.; Quignard. F.; Choplin, A.; Olivier, D.; Basset, J.-M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1660. (b) d'Ornelas, L.; Reyes, S.; Quignard, F.; Choplin, A.; Basset, J.-M. *Chem. Lett.* **1993**, 1931. (c) Corker, J.; Lefebvre, F.; Lecuyer, C.; Dufaud, V.; Quignard, F.; Choplin, A.; Evans, J.; Basset, J.-M. *Science* **1996**, *271*, 966. (d) Dufaud, V.; Basset, J.-M. *Angew. Chem., Int. Ed. Engl. 1998*, **37**, 806.

214. (a) Weiss, M. J.; Hagedorn, C. J.; Mikesell, P. J.; Little, R. D.; Weinberg, W. H. *J. Am. Chem. Soc.* **1998**, *120*, 11812. (b) Hagedorn, C. J.; Weiss, M. J.; Weinberg, W. H. *J. Am. Chem. Soc.* **1998**, *120*, 11824.

215. Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85.

216. (a) Pardy, R. B. A.; Taylor, M. J.; Constable, E. C.; Mersh, J. D.; Sanders, J. K. M. *J. Organomet. Chem.* **1982**, *231*, C25. (b) Brookhart, M.; Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc., Chem. Comm.* **1983**, 691. (c) Cracknell, R. B.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Comm.* **1984**, 326. (d) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443. (e) Cracknell, R. B.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Comm.* **1986**, 1005. (f) Brookhart, M.; Lincoln, D. M.; Volpe, A. F., Jr.; Schmidt, G. F. *Organometallics* **1989**, *8*, 1212. (g) Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5634. (h) Brookhart, M.; Lincoln, D. M.; Bennett, M. A.; Pelling, S. *J. Am. Chem. Soc.* **1990**, *1990*, 2691. (i) Brookhart, M.; Grant, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 2151. (j) Brookhart, M.; DeSimone, J. M.; Grant, B. E.; Tanner, M. J. *Macromolecules* **1995**, *28*, 5378. (k) Lenges, C. P.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 3165.

217. Wehrli, F. W.; Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*, Heyden & Son Ltd; Bristol, 1978.

218. Marvell, E. N. *Thermal Electrocylic Reactions*, Academic Press; New York, 1980, pp182-183.

219. (a) Pinhas, A. R.; Samuelson, A. G.; Risemberg, R.; Arnold, E. V.; Clardy, J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 1668. (b) Bruce, M. I.; Duffy, D. N.; Liddell, M. J.; Tiekink, E. R. T.; Nicholson, B. K. *Organometallics* **1992**, *11*, 1527. (c) Trost, B. M.; Tanoury, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 1636. (d) Chen, Q.; Sioma, C.; Kan, S. Z.; Freiser, B. S. *Int. J. Mass. Spectrom.* **1988**, *179/180*, 231.

220. Migratory insertion of a metal carbene into a metal vinyl bond: Selnau, H. E.; Merola, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 4008. Migratory carbene insertion into metal alkyl bonds: Casty, G. L.; Stryker, J. M. *Organometallics* **1997**, *16*, 3083 and references therein.

221. (a) Casey, C. P.; Brady, J. T. *Organometallics* **1998**, *17*, 4620. (b) Casey, C. P.; Brady, J. T.; Boller, T. M.; Weinhold, F.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 12500 and refereneces therein.

222. Pertici, P.; Vitulli, G.; Paci, P.; Porri, L. *J. Chem. Soc., Dalton Trans.* **1980**, 1961.

223. Baldwin, J. E.; Belfield, K. D. *J. Org. Chem.* **1987**, *52*, 4772.

224. Fe: (a) Zou, C.; Wrighton, M. S.; Blaha, J. P. *Organometallics* **1987**, *6*, 1452. (b) Hamon, P.; Hamon, J-R.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1992**, 1602.

225. $Cp^*_2M$: Co: (a) Schneider, J. J.; Goddard, R.; Werner, S.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1124. (b) Schneider, J. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1392. Rh: (c) Cloke, F. G. N.; Day, J. P.; Greenway, A. M.; Seddon, K. P.; Shimran, A. A.; Swain, A. C. *J. Organometal. Chem.* **1989**, *372*, 231. (d) Gusev, O. V.; Denisovich, L. I.; Peterleitner, M. G.; Rubezhov, A. Z.; Ustynyuk, N. A.; Maitlis, P. M. *J. Organometal. Chem.* **1993**, *452*, 219.

226. Ustynyuk, N. A.; Peterleitner, M. G.; Gusev, O. V.; Denisovich, L. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1993**, 1802. Engl. Translation: *Bull. Acad. Sci. USSR* **1993**, 1727. see also reference 125.

227. (a) Balakrishnan, P. V.; Maitlis, P. M. *J. Chem. Soc. (A)* **1971**, 1715. (b) Gusev, O. V.; Morozova, L. N.; Peganova, T. A.; Petrovskii, P. V.; Ustynyuk, N. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1994**, 514. Engl. Translation: *Bull. Acad. Sci. USSR* **1994**, 474. (c) Gusev, O. V.; Morozova, L. N.; Peganova, T. A.; Petrovskii, P. V.; Ustynyuk, N. A.; Maitlis, P. M. *J. Organometal. Chem.* **1994**, *472*, 359.

228. Balakrishnan, P. V.; Maitlis, P. M. *J. Chem. Soc. (A)* **1971**, 1721.

229. van Tamelen, E. E.; Brauman, J. I.; Ellis, L. E. *J. Am. Chem. Soc.* **1971**, *93*, 6145.

230. Boag, N. M., Personal communication.

231. Green, M. L. H.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3753.

232. Halocarbons: Herberich, G. E.; Bauer, E. *J. Organometal. Chem.* **1969**, *16*, 301. (b) Herberich, G. E.; Bauer, E. J.; Schwarzer, J. *J. Organometal. Chem.* **1969**, *17*, 445.

233. $R_2Cd$: Razuvaev, G. A.; Mar'in, V. P.; Vyshinskaya, L. I.; Grinval'd, I. I.; Spiridonova, N. N. *Zh. Obsh. Khim.*, **1987**, *57*, 1773. English translation: p1583. (b) Razuvaev, G. A.; Mar'in, V. P.; Andrianov, L. I.; Vyshinskaya, L. I.; Druzhkov, O. N. *J. Organometal. Chem.* **1987**, *346*, 403.

234. $R_3Al$: Gaudet, M. V.; Hanson, A. W.; White, P. S.; Zaworotko, M. J. *Organometallics* **1989**, *8*, 286.

235. RLi: (a) Fischer, E. O.; Herberich, G. E. *Chem. Ber.* **1961**, *94*, 1517. (b) Fischer, E. O.; Fellmann, W.; Herberich, G. E. *Chem. Ber.* **1962**, *95*, 2254. (c) Furlani, C.; Collamati, I. *Chem. Ber.* **1962**, *95*, 2928. (d) Churchill, M. R.; Mason, R. *Proc. Roy. Soc. London. Ser. A.* **1964**, *279*, 191. (e) Tane, J. P.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 617. See also (f) Malkov, A. V.; Petrovskii, P. V.; Fedin, E. I.; Leonova, E. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 1270. Engl. Translation: *Bull. Acad. Sci. USSR* **1987**, 1169. (g) Maryin, V. P.; Petrovskii, P. V. *J. Organometal. Chem.* **1992**, *441*, 125. See also reference 93f. Addition of RLi to decamethylcobaltocinium: (h) Razuvaev, V. P.; Mar'in,

V. P.; Vishinskaya, L. I.; Mal'kova, G. Y.; Andrianov, Y. U.; Druzhkov, O. N. *Dokl. Akad. Nauk SSSR* **1987**, *294*, 614. English translation p 246.

236. (a) Halpern, J.; Okamoto, T.; Zakhariev, A. *J. Mol. Catal.* **1976**, *2*, 65. (b) Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 838. (c) Chan, A. S. C.; Pluth, J. J.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 5952. (d) Halpern, J. *Inorg. Chim. Acta.* **1981**, *50*, 11. (e) Halpern, J.; Riley, D. P.; Chan, A. S. C.; Pluth, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 8055. (f) Halpern, J. *Science* **1982**, *217*, 401. (g) Landis, C. R.; Halpern, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 1746.

237. Koelle, U.; Sistig, F.; Gersdorf, J. *J. Organomet. Chem.* **1982**, *233*, 253.

238. (a) Nagashima, H.; Matsuda, H.; Itoh, K. *J. Organomet. Chem.* **1983**, *258*, C15. (b) Itoh, K.; Mukai, K.; Nagashima, H.; Nishiyama, H. *Chem. Lett.* **1983**, 449.

239. (a) Katz, T. J.; Sudhakar, A.; Teasley, M. F.; Gilbert, A. M.; Geiger, W. E.; Robben, M. P.; Wuensch, M.; Ward, M. D. *J. Am. Chem. Soc.* **1993**, *115*, 3182. (b) Gilbert, A. M.; Katz, T. J.; Geiger, W. E.; Robben, M. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 3199.

240. $(C_5Me_5)Co(\eta^4\text{-}C_6H_8)$ was prepared by heating a solution of $Cp^*Co(C_2H_4)_2$ and 1,3-cyclohexadiene in hexane at 65°C for 12 h.

241. $(C_6Me_6)Ru(\eta^4\text{-}C_6H_8)$: (a) Bennett, M. A.; Metheson, T. W. *J. Organomet. Chem.* **1978**, *153*, C25. (b) Bennett, M. A.; Huang, T.-N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74.

242. Cp*H: Threlkel, R. S.; Bercaw, J. E.; Siedler, P. F.; Stryker, J. M.; Bergman, R. G. *Org. Synth.* **1987**, *65*, 42.

243. Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892.

244. Ball, R. G.; Graham, W. A.; Heinekey, D. M.; Hoyano, J. K.; McMaster, A. D.; Mattson, B. M.; Sichel, S. T. *Inorg. Chem.* **1990**, *29*, 2023.

245. (a) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 99. (b) Sheats, J. E. *J. Organomet. Chem. Lib.* **1979**, *7*, 461.

246. (a) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849. See also: (b) Martin, J.; Fauconet, M.; Moise, C. *J. Organomet. Chem.* **1989**, *371*, 87 and references therein.

247. (a) Hart, W. P.; Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 1196. (b) Macomber, D. W.; Hart, W. P.; Rausch, M. D. *Adv. Organomet. Chem.* **1982**, *21*, 1. (c) Hart, W. P.; Shihua, D.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *282*, 111.